

# Birla Central Library

PILANI (Jaipur State)

Class No :- 667.2

Book No :- K83M v.2

Accession No - 33761







A

MANUAL OF DYEING

CHARLES GRIFFIN & CO., LTD., PUBLISHERS

## TEXTILE ANALYSIS. A Text-Book for Students, covering all materials and allied elements.

By S. R. TROTMAN, M.A., F.I.C., and E. R. TROTMAN, Ph.D., M.Sc., A.I.C.

Medium 8vo. Cloth. Pp. i-vi + 301. With 57 Illustrations 24s.

Contents: The Identification and Determination of Textile Fibres—Physical Tests for Textile Materials—Determination of Specific Gravity and Viscosity—Standard Volumetric Solutions—Analysis of Organic Compounds—Acids—Indicators and their Hydrogen-ion Concentrations—Alkalies—Bleaching Agents—Water and Effluents—Analysis of Fibres—Oils—Organic Solvents—Formaldehyde, Tannins—Blueing Agents, Glycerol—Starch, Dextrin Glue, Gelatin, Casein, and Vegetable Gums—Metallic Salts—Nitro-compounds, Amines and Phenols—The Detection and Analysis of Dyestuffs.—Index.

"A most welcome addition to the bookshelf of every textile technologist."—*Textile Recorder*.

## THE PRINCIPLES AND PRACTICE OF TEXTILE PRINTING.

By E. KNECHT, Ph.D., M.Sc., F.I.C., and J. B. FOTHERGILL.

Third Edition. Revised Throughout and Enlarged by J. B. FOTHERGILL. In Medium 8vo. Cloth. Pp. i-xxii + 1,048. With 19 Plates, 90 Illustrations, and 221 actual printed fabric Patterns, inset in Text 80s.

Contents: PART I: Introduction II: Methods of Printing III: Preparation of Cloth for Printing IV: Preparation of Colours for Printing V: Treatment of Goods after Printing. VI: Mordants VII: Styles of Printing: (a) Direct (b) Dyed, (c) Azolic Colours, (d) Discharge, (e) Reserve (Resist), (f) Raised, (g) Printing of Linings (Paste Colours), (h) Metal Printing, (i) Crepon or "Crimp" VIII: Finishing of Printed Calicoes. IX: Wool and Half-Wool Printing X: Silk and Half-Silk Printing XI: Printing of Artificial Silks—Appendix.—Index

"The book undoubtedly becomes the standard work on the subject, and we can recommend it heartily to the consideration of our readers" —*Textile Manufacturer*

## THE BLEACHING AND FINISHING OF COTTON.

By S. R. TROTMAN, M.A., F.I.C., and E. L. THORP, A.C.G.I., A.M.I.E.E.

Third Edition. Thoroughly Revised, Enlarged, and Re-set. In Large 8vo. Cloth. Pp. i-x + 688. With 240 Illustrations 35s.

Contents: Introduction—The Nature, General Properties, and Classification of Textile Fibres—Natural History of Cotton—Varieties and Classification of Commercial Cotton—Blending, Buying, and Spinning—Vegetable Cells—The Structure of the Cotton Hair—Variations in Structure—Unripe, Dead, and Abnormal Hairs—The Constituents of Cotton—Proteins and Amino Compounds—Colloids—The Determination of Proteins—Oils, Fats, and Waxes—Pectose and Pectin Colouring Matter—Mineral Matter—Tannic Acid—The Carbohydrates and Cellulose—Hydrocellulose and Oxycellulose—Special Properties of Cotton—Artificial Silk—Micro-organisms and their Action on Cotton—Water—Water Softening—Industrial Analysis of Water—The Physical and Chemical Properties of Cotton Yarns and Fabrics—Cotton Piece Goods (Introductory)—Steeping—Transmission of Cloth—Impregnation and Plaiting—Alkali Boiling—General Considerations—Kiers—Chemicals—Organic Solvents—Washing Machines—Bleaching Agents, Sulphur Dioxide and its Derivatives—Chlorine and its Derivatives—Bleaching Powder—The Bleaching Process—Souring—Sodium Hypochlorite, Chlorous Acid, Chloric Acid, Perchloric Acid—The Non-chlorinated Oxidising Bleaching Agents—Processes—Stains, Discoloration, and Damages—Finishing and the Materials used in Finishing—Mangling, Drying, and Conditioning—Stiffening—Auxiliary Machines and Processes—Scenters—Beetling—Calendering—Combined Finishing Processes.—Index  
"Deserves the attention of practical bleachers, and we can recommend it to them with confidence."—*Textile Mercury*

CHARLES GRIFFIN & CO., LTD., 42 DRURY LANE, LONDON, W.C. 2

A

# MANUAL OF DYEING:

FOR THE USE OF PRACTICAL DYERS, MANUFACTURERS,  
STUDENTS, AND ALL INTERESTED IN THE  
ART OF DYEING.

EDMUND KNECHT,

PH.D. (ZÜRICH), M.SC. TECH (MANCHESTER), F.I.C.,  
PROFESSOR OF TECHNOLOGICAL CHEMISTRY, VICTORIA UNIVERSITY OF  
MANCHESTER, AND HEAD OF THE CHEMICAL DEPT., MUNICIPAL  
SCHOOL OF TECHNOLOGY, MANCHESTER EXAMINER  
IN DYEING TO THE CITY AND GUILDS OF LONDON  
INSTITUTE; EDITOR OF *The Journal of the  
Society of Dyers and Colourists*.

BY *W. H. A.*

CHRISTOPHER RAWSON,

F.I.C., F.C.S.,  
ANALYTICAL AND CONSULTING CHEMIST; SOMETIME HEAD OF  
THE CHEMISTRY AND DYEING DEPT., TECHNICAL  
COLLEGE, BRADFORD, VICE PRESIDENT  
OF THE SOCIETY OF DYERS  
AND COLOURISTS.

AND

RICHARD LOEWENTHAL, PH.D. (MUNICH),

TECHNICAL CHEMIST AND COLOURIST, SOMETIME HEAD OF THE DYEING AND FINISHING DEPARTMENT OF THE  
ROYAL WEAVING SCHOOL, COTTESB.

**Third Edition.**

(Reprinted)

COMPLETE IN TWO VOLUMES WITH NUMEROUS ILLUSTRATIONS,  
AND FIVE PLATES.

**VOL. II.**

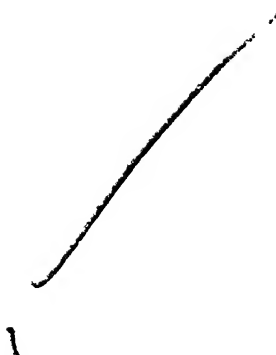


LONDON:  
CHARLES GRIFFIN AND COMPANY, LIMITED:

42 DRURY LANE, W.C.2.

1941

[All Rights Reserved.]



2

667.2  
1083 M  
V.2

3576

6186 C/H  
61

VOL. II.



PART VII.

## ABBREVIATIONS (PART VII).

---

<b>B. A. S. F.</b>	=	<b>Badische Anilin- und Soda-Fabrik, Ludwigshafen-on-Rhine.</b>
<b>Basle Ch. Works</b>	=	<b>Basle Chemical Works, Basle.</b>
<b>Bayer</b>	=	<b>Farbenfabriken, vorm. Fr. Bayer &amp; Co., Elberfeld.</b>
<b>Berlin</b>	=	<b>Action Gesellschaft fur Anilin-Fabrikation, Berlin.</b>
<b>Cassella</b>	=	<b>Leopold Cassella &amp; Co., G. m. b. H., Frankfort-on-Maine.</b>
<b>Ch. Ind. Basle</b>	=	<b>Society of Chemical Industry, Basle.</b>
<b>Claus &amp; Co.</b>	=	<b>Droylsden, near Manchester.</b>
<b>Clayton</b>	=	<b>The Clayton Aniline Co., Manchester.</b>
<b>Dahl</b>	=	<b>Wuelfing, Dahl &amp; Co., Act.-Ges., Barmen.</b>
<b>Durand</b>	=	<b>L. Durand, Huguennin &amp; Co., Basle.</b>
<b>Geigy</b>	=	<b>Aniline Colours and Extract Works, formerly J. R. Geigy, Basle.</b>
<b>Holliday</b>	=	<b>Read Holliday &amp; Sons, Ltd., Huddersfield.</b>
<b>Kalle</b>	=	<b>Kalle &amp; Co., Act.-Ges., Biebrich-on-Rhine.</b>
<b>Leonhardt</b>	=	<b>Farbwerk Mulheim, formerly A. Leonhardt &amp; Co., Mulheim in Hessen.</b>
<b>Lepetit</b>	=	<b>Lepetit &amp; Dollfuss, Susa, Italy.</b>
<b>Levinstein</b>	=	<b>Levinstein, Ltd., Manchester.</b>
<b>Weiler ter Meer</b>	=	<b>Chemische Fabriken, vorm. Weiler ter Meer, Uerdingen on-Rhine.</b>
<b>M. L. B.</b>	=	<b>Farbwerke, vorm. Meister, Lucius &amp; Bruning, Hoechst-on-Maine.</b>
<b>Monnet</b>	=	<b>Gilliard, P. Monnet &amp; Cartier, Lyons.</b>
<b>Oehler-Griesheim</b>	=	<b>Chemische Fabrik Griesheim-Electron, Griesheim-on-Maine.</b>
<b>Poirrier</b>	=	<b>Société Anonyme des Matières Colorantes (A. Poirrier &amp; G. Dalsace), Paris.</b>
<b>Sandoz</b>	=	<b>Sandoz Chemical Works, Basle.</b>
<b>Schoellkopf</b>	=	<b>The Schoellkopf Aniline and Chemical Co., Buffalo.</b>
<b>Thann</b>	=	<b>Fabriques de Produits Chimiques de Thann et de Mulhouse.</b>

## PART VII.

## ARTIFICIAL ORGANIC COLOURING MATTERS.

A NEW age was inaugurated for the art of dyeing by Perkin's discovery of Mauve in 1856. Almost numberless colouring matters have since been produced from coal-tar; relatively few have stood the test of time, and many of these may possibly disappear from commerce before another half-century has passed; but science works indefatigably, and enriches us continuously with new and better, with more permanent and beautiful colouring matters, and so will gradually succeed in promoting the dyeing industry to the highest state of perfection.

The constitution of most artificial dyestuffs being well known, scientists have attempted to show the relations between their constitution and tinctorial properties.

As far back as 1868, Græbe and Liebermann expressed the opinion that it is chiefly an intimate connection of the atoms of oxygen and nitrogen which gives rise to the colouring character of organic compounds, and that the colouring character is destroyed if the intimate connection is loosened by the entrance of hydrogen (*leuco-compounds*). Thus,

Benzo quinone ( $C_6H_4 < \begin{smallmatrix} O \\ \diagdown \diagup \\ O \end{smallmatrix} >$ ) is yellow.

Hydroquinone ( $C_6H_4 < \begin{smallmatrix} O-H \\ \diagdown \diagup \\ O-H \end{smallmatrix} >$ ) is colourless.

Azobenzene ( $C_6H_5-N=N-C_6H_5$ ) is yellowish-red;

Hydrazobenzene ( $C_6H_5-N-N-C_6H_5$ ) is colourless.



Although Græbe and Liebermann's views were pronounced long ago, when our knowledge of the chemical constitution of the dyestuffs was still very limited, they constitute the basis of the modern views of the tinctorial character of organic compounds.

O. N. Witt published in 1876 a more comprehensive theory of the constitution of dyestuffs. According to this author a colour-bearing (*chromophorous*) group or *chromophor* must be introduced into the colourless aromatic hydrocarbons to render them capable of yielding a coloured substance. Benzene is colourless, but mononitrobenzene,  $C_6H_5NO_2$ , dinitrobenzene,  $C_6H_4(NO_2)_2$ , and trinitrobenzene,  $C_6H_3(NO_2)_3$ , are coloured and so is azobenzene,  $C_6H_5N=NC_6H_5$ . Those compounds which contain chromophorous groups and are coloured, but possess little dyeing power, are called by Witt *chromogenes*; because they are able to generate colouring matters by taking up salt-forming groups. Thus the chromogene trinitrobenzene becomes the dyestuff trinitrophenol or picric acid,  $C_6H_2(NO_2)_3(OH)$ , by the entrance of the hydroxyl-group "OH"; azobenzene is converted into the dyestuff amidoazo-



benzene (Aniline yellow),  $C_6H_5N=NC_6H_4NH_2$ , by the amido-group "NII." These salt-forming groups are termed by Witt *auxochromous* groups. The dyestuffs are less coloured in the free state than in the form of salts; while the solution of picric acid is light yellow, that of sodium picrate is dark yellow; and the solution of amidoazobenzene is yellow, while that of amidoazobenzene hydrochloride is purplish. The entrance of the amido-group into the trinitrobenzene does not convert the same into a dyestuff, because its basic influence is destroyed by the acid character of the nitro-groups. The sulpho-group,  $SO_3H$ , and the carboxyl-group,  $CO_2H$ , although salt-forming, are not auxochromous groups, because they convert the chromogenes into weak dyestuffs only. Witt established the following principles:—

1. The tinctorial character of an aromatic substance depends on the simultaneous presence of an auxochromous and a chromophorous group

2. The chromophor exerts the colour-generating influence more in the salt-like compounds of the dyestuffs than in the free compounds.

3. Of two dyestuffs of analogous constitution that one is the better the salts of which are the more stable.

In various recent books the dyestuffs have been classified according to the chromophors, and this division appears the best for a scientific treatise on the colouring matters. It is, however, necessary in this case to separate substances which are closely related in their behaviour towards the fibres and to bring together bodies which are quite different in their general tinctorial character. We believe it to be more appropriate for a practical handbook of dyeing to divide the materials in respect to those properties which are most important to the dyer, and to describe together those dyestuffs which behave similarly in dyeing and are used in the same way and in combination with each other. Although this division is not ideal and consistent in every case (since many dyestuffs are used in different ways), it seems to us to be the most convenient for practical purposes.

In the sequel, the dyestuffs will be described in the following groups\* :—

I. *Direct Cotton Colours* or *Salt Colours*.—Colours which in a neutral or slightly alkaline bath containing salt (common salt or Glauber's salt) dye cotton in full shades without the aid of mordants.

II. *Sulphide Colours* or *Sulphur Colours*.—Colours which are dissolved with the aid of sodium sulphide and dye cotton in full shades without the aid of mordants from a sulphide bath.

III. *Basic Colours*.—Colours of a basic nature which dye animal fibres without mordants. They form tannates, insoluble in water, and dye the vegetable fibres with the aid of tannin mordants.

IV. *Eosins* and *Rhodamines*.

V. *Acid Colours*.—Salts of colour acids which dye the animal fibres without the aid of mordants, but as a rule only with the aid of acid.

VI. *Mordant Colours*.—Colours which are dyed with the aid of *metallic* mordants. (Alizarins and others.)

VII. *Acid Chrome Colours*.—Colours which are dyed in an acid-bath on wool and developed and fixed with the aid of chrome mordants.

VIII. *Miscellaneous Colours* :—

(a) Aniline black.

(b) Indigo and other vat dyes.

(c) Insoluble azo-colours (ice-colours).

\* Generally, the dyestuffs will be described in the different groups according to the order of the colours of the rainbow. But we have not strictly followed this principle, if it seemed advisable to place similar compounds together; and in the group of the acid colours we have begun with yellow.

In the following description of the dyestuffs it has been thought expedient, on account of the great number of substances, to give their characteristic properties as briefly as possible. Their properties are given in the following order:—(1) The appearance of the dyestuffs; (2) the appearance of the aqueous solution; (3) the action of hydrochloric acid, indicated by the symbol HCl, on this solution; (4) the action of strong caustic soda lye, NaOH, on a strong aqueous solution of the dyestuff—the words “soluble precipitate” signify that the precipitate dissolves in pure water; (5) the colour of the solution of the dyestuff in sulphuric acid (monohydrate); and, finally, (6) the reaction which is noticed on diluting the solution with water. The other properties of the various dyestuffs will be described as far as they appear to be important in every special case.

The constitution of the azo-compounds has been briefly indicated by naming first (on the left side) the diazotised base, and then (on the right side) the other compounds on which the diazotised base acts.

## DIRECT COTTON COLOURS.

A great number of dyestuffs have been brought into commerce during the last twenty years which are distinguished by the common property of dyeing the vegetable fibres in full shades, and fairly fast to washing without the aid of mordants. The first of these substances, used in this way, was *Congo-red*, which was discovered in 1884 by Böttiger; hence the whole group, especially the derivatives of benzidine and tolidine, which are chemically related to this dyestuff, are frequently called the “Congo-colours” or “benzidine-colours.”

The direct cotton colours which are found in commerce at the present time are, without exception, sulphonates of sodium, ammonium, or potassium.

Most of them are tetrazo-compounds—i.e., compounds which contain the azo-group— $\text{N}=\text{N}$ —twice in the molecule.

Azo-compounds which contain only one group— $\text{N}=\text{N}$ —in the molecule (like the bulk of the acid colours), do not dye cotton without the aid of mordants, with the exception of the derivatives of certain thio-bases (see below).

It would appear from this fact that the direct dyeing character of these compounds is due to the double chromophorous group  $\left\{ \begin{array}{l} -\text{N}=\text{N}- \\ -\text{N}=\text{N}- \end{array} \right.$ . Not all tetrazo-colours, however, dye unmordanted cotton equally well.

Like the ordinary azo-colours, the tetrazo-colours are produced by the action of diazotised amines on phenols (naphthols) or aromatic amines or their sulphonic or carboxylic acids; thus they contain, in addition to the double chromophorous group  $\text{N}=\text{N}$ , the auxochromous groups “ $\text{NH}_2$ ” or “ $\text{OH}$ ”; or their derivatives, like “ $\text{NH}(\text{C}_6\text{H}_5)$ ” or “ $\text{OC}_2\text{H}_5$ .”

The tetrazo-colours are derivatives of benzidine or tolidine (Congo-colours), diamidostilbene, azoxydiamines, and various other diamines. Various kinds of tetrazo-colours—e.g., the Benzo fast scarlets—are prepared by special methods.

In addition to the tetrazo-colours, a class of direct cotton colours is known, which are either not azo-compounds at all, or the tinctorial character of which is not due, in the first place, to their azo-group. The dyestuffs of this group are obtained from compounds, which are prepared by heating organic bases, notably paratoluidine and metaxylidine, with sulphur. In this way “thio-bases” are obtained, the chromophorous group of which has

the constitution— $\left\langle \begin{array}{c} \text{S} \\ \text{N} \end{array} \right\rangle \text{C}$ —. The first of these compounds was *Primuline*,

discovered by A. G. Green. Neither Primuline nor the similar colouring matter named *Thioflavine S*, are azo-compounds. Several other dyestuffs—*e.g.*, *Erika*, *Cotton yellow R*, and, in a certain sense, also *Thiazol yellow*, are azo-compounds; but undoubtedly they possess the same chromophorous group as Primuline, so that the azo-group need not be considered as an essential condition for the colouring character of the compound.

Further, some yellow, orange, and brown dyestuffs belong to the group of direct cotton colours, which are obtained by the action of alkalies on nitro-toluene sulphonic acid, and are derivatives of stilbene, such as the Mikado colours, Chicago orange, Direct yellow R, Diamine fast yellow A, &c. They dye cotton very well, and are distinguished by their very low affinity with the animal fibre in the presence of alkalies, by reason of which property they are exceedingly well suited for dyeing mixed goods consisting of cotton and either wool or silk. According to the recent researches of A. G. Green, all these stilbene colours are azo-compounds.\*

The nature of the process of dyeing the vegetable fibres with these colours has not yet been explained, and no chemical reaction has been discovered to take place in the dye-bath. The cotton absorbs the dyestuff by some cause, generally termed affinity (diffusion by Mueller-Jacobs; solution by O. N. Witt), and retains it with a considerable power. The colour is extracted from the fibre by water, and can be stripped to a large degree by repeated boiling out with water. Inversely, in dyeing, a part of the colouring matter is always retained by the dye-liquor, the quantity of which depends on the dissolving power of the dye-liquor and on the absorbing capacity of the fibre in regard to the dyestuff. If the former is very great—*i.e.*, if a great quantity of water is used—a large proportion of colouring matter is retained by the dye-liquor; if the latter is considerable—*i.e.*, if much material (compared with the amount of liquid) or, to use the common expression, if concentrated or "short" baths are used—the liquor is better exhausted. The dissolving power of the liquor can be diminished not only by decreasing the quantity of water, but also by adding soluble salts, notably common salt and Glaubersalt, also phosphate of soda, &c. Common salt and Glaubersalt diminish the dissolving power of water towards the dyestuffs (as is the case in the well-known process of "salting out"), and phosphate of soda acts in the same way, whereas potash and soda chiefly serve for correcting the hardness of the water and to keep the dyestuffs well dissolved. The influence of these salts, however, has not been studied except from a mere practical point of view. It may be observed that the levelling of these dyestuffs is improved by the addition of such fatty salts as ordinary soap, Turkey-red oil, Monopol soap, Monopol oil, &c, and also by such feebly alkaline salts as borax, in addition to potash and soda named above.

On account of these circumstances cotton is dyed with the direct cotton colours in as concentrated a bath as possible, and with the addition of varying quantities of certain salts. The amount of the latter should not be so large as to precipitate the dye, as it is absolutely necessary, to prevent uneven dyeing, that it be entirely in solution.

The property of these dyestuffs to redissolve readily in water and to go on the fibre easily, prevents them from accumulating in any part of the material in unequal quantities; hence they dye the vegetable fibres very evenly. The direct cotton colours possess the property of "level dyeing" and "running" to such a degree that in many cases two hanks of cotton, one dyed with one of these dyestuffs and the other being white, when boiled together for a length of time in water, will acquire approximately the same shade.

The nature of the process taking place in dyeing wool and silk with the direct cotton colours has not been studied; it resembles to some extent the

\* *Journ. Soc. Dyers and Col.*, 1907, p. 162.

dyeing of the "acid colours," since these dyestuffs are taken up most rapidly from acid-baths by the animal fibres. On the other hand, the animal fibres may be dyed very well in neutral or even weakly alkaline baths.

The direct cotton colours possess the property of forming lakes with the basic colours. E. Knecht\* and G. Galland† have studied this reaction, which was first made known in the case of Chrysamín by the *Farbenfabriken*, vorm. Fr. Bayer & Co. They found that only the basic colours form lakes with those dyestuffs, and that many of the lakes are decomposed above 70° and even at lower temperatures. The composition of some of these lakes has been investigated by E. Baenziger and L. E. Vliess.‡

This property of forming lakes is largely utilised to produce compound shades by first dyeing with a direct colour and subsequently topping with a basic colour.

**APPLICATION OF THE DIRECT COTTON COLOURS.**—The direct cotton colours are used for the dyeing of unmordanted cotton. In calico-printing their property of bleeding prevents them from being extensively used for direct printing. They are employed, however, for padding and bottoming and for discharged styles. They also find employment in the dyeing of artificial silk, linen, jute, and the animal fibres.

These colours are dyed in neutral or alkaline baths, especially on the vegetable fibres. They can be used in admixture with each other and dyed in the same bath, to produce compound shades. As a rule, these dyestuffs are precipitated by lime, but especially by magnesia; hence magnesian or calcareous water should be avoided or corrected. The best way to purify hard water for dyeing with these colours, is to add some soda ash and boil, whereby the lime or magnesia will be precipitated in an insoluble innocuous form. All these colours are soluble in water, some indeed rather sparingly, but freely enough to admit of their application in aqueous solutions.

The general mode of procedure is to prepare the bath with a solution of the whole amount of the dyestuff required and with the necessary other ingredients. As little water as possible is used, and the bath should be heated with a steam coil, not with direct steam.

In the case of calcareous water the liquor is boiled with some soda as indicated above, before the colour solution is added. The goods are entered into the fully prepared bath at a medium or high temperature and turned from time to time during 30 to 60 minutes. As a rule, the dyeing takes place at the boil. When no more colour is taken up, the goods are removed from the bath, wrung, and then rinsed in cold water, soda solution or Turkey-red oil (see below), and dried. The dye-baths are not exhausted and may be used continuously; their strength is restored after each dyeing by adding as much of the ingredients as has been consumed (approximately  $\frac{1}{3}$  of the original amount).

The direct cotton colours are stripped more or less easily from the fibres, especially from cotton and linen, by water and soap solutions; and are liable to tinge white fibres with which they come in contact in the same bath. This property of *bleeding* or *running* is very objectionable, and largely prevents their use in calico-printing and linen dyeing. In spite of this fact, however, their shades lose comparatively little in intensity on repeated soaping, and they are considered to be moderately fast, or even fairly fast to soap.

In the special description of the dyestuffs attention will not be called in each case to the property of "bleeding," as it is common to some extent to all these colours.

Many of the direct cotton colours are very fugitive to light and certainly

\* *Journ. Soc. Dyers and Col.*, 1886, p. 2.

† *Ibid.*, 1886, p. 145.

‡ *Ibid.*, 1899, p. 148.

not faster than the bulk of the basic colours, whereas a good number, such as Diamine fast red, Diamine and Benzo fast blues, and others, possess a very good fastness, and some, like Chrysamin, Chrysophenin, Diamine fast yellow B, Oxyphenin, &c., belong to the fastest colours known. Generally they are less fugitive on the animal than on the vegetable fibres.

Some of the direct cotton colours, especially Congo red, are more or less sensitive towards the action of dilute acids, even of the acids present in the atmosphere of towns, their shades being thereby turned blue or brownish; this defect may be overcome to a certain extent by charging the dyed fibre with soda or some other non-volatile alkali (see below). Some shades, particularly the yellow shades, are reddened by the action of dilute alkalis. The original shades, whether they have been changed by acids or alkalis, are easily restored by washing with water or by treatment with a very diluted counteracting chemical agent (ammonia or acetic acid respectively).

The topping of the direct cotton colours with basic dyestuffs, which has been previously mentioned, takes place in the most simple manner; the goods, after having been dyed with the direct colours, are wrung out and slightly rinsed in water (to prevent rubbing) and then worked in a tepid bath of the basic colour until the desired shade is obtained, washed, and dried. Elevated temperatures spoil the shade by decomposing the lake which is formed by the two colours. The direct colours lose in some cases the property of bleeding by this topping process, being converted into insoluble compounds.

A great number of direct cotton colours are capable of being diazotised on the fibre and forming azo-compounds with phenols, amines, &c. (Primuline ingrain colours, Diamine blacks, &c.). These new compounds, being insoluble, do not bleed much, and their formation on the fibre is a valuable method of producing shades which are fast to soap. This method of *diazotising and developing* new colours on the fibre was discovered by A. G. Green in 1888.\*

Chemically related to this process of diazotising and developing is the so called *coupling process*, which consists in the treatment of certain direct cotton colours on the fibre with cold solutions of diazo-compounds, especially that of paranitraniline, and yields very full and deep brown and black, and recently also some other very good shades fast to washing and acid cross-dyeing.

A great many of the direct cotton colours are materially improved in fastness by an *after-treatment with metallic salts*. Hot solutions of copper sulphate improve chiefly the fastness to light and to a certain extent also that to washing of some colours. This fact was first described by the *Farbenfabriken vorm. Fr. Bayer & Co.* (British patent, 1889, No. 3934) in connection with certain derivatives of dianisidine and sulphonic acids of naphthol (Azurines), but has also proved valuable for many other dyestuffs. In addition to copper salts, those of zinc, nickel, cobalt, iron, and chromium have also been recommended; but of the latter only those of chromium, and still more so the bichromates of potash and soda have become important by their property of improving the fastness to washing of some products, such as Chrysamin, Diamine green G, and Diamine jet black. A hot mixture of copper sulphate and bichromate of potash improves the fastness to washing and to light of such colours as Benzochrome brown, Chromanil black, Diamine catechine, &c. The fastness to water of most colours of this group is improved by a short treatment with alum, aluminium acetate, or other aluminium salts, or with a warm solution of formaldehyde.

*Note.*—Some of the diazotised or coupled colours are also improved by a treatment with blue vitriol, which may be added to the diazotising or coupling liquor, although the effect is more intense when applied by a separate hot bath.

\* *Journ. Soc. Dyers and Col.*, 1888, p. 40.

**DYEING OF COTTON WITH THE DIRECT COTTON COLOURS.**—These colours are usually dyed on unbleached cotton, fuller shades being obtained thereon compared with bleached cotton. The cotton is simply boiled in water or in an alkaline liquor to wet it thoroughly and to prepare it for taking up the colours evenly; and for very pale shades only is bleaching of the material previous to dyeing necessary. An addition of Turkey-red oil, Monopol oil, Monopol soap, &c., assists the wetting. Mercerised cotton possesses greater affinity for these colours than ordinary cotton, and assumes under similar conditions a considerably deeper shade, the difference amounting to one-fourth or one-fifth.

The general method of dyeing is as follows:—The bath is prepared with the requisite ingredients, the colour is added at once, and the material is entered at or near the boiling point, and dyed at these temperatures for three-quarters to one hour, a high temperature of the bath being beneficial for the fastness to washing. The colours may, however, be very well dyed also at moderate temperatures or even in the cold. For pale shades the dyeing should begin in a tepid bath. Frequently the cotton is turned in the boiling liquor for about half an hour only, and then allowed to “feed” in the cooling bath. The bath not being exhausted is used as concentrated as possible, and kept for continuous use. In order to prevent dilution of the liquor by condensed steam it is best to heat the bath by a closed steam coil. Calcareous water may be easily corrected by boiling it with  $\frac{1}{4}$  to  $\frac{1}{2}$  grm. soda ash per litre ( $\frac{1}{2}$  to 1 oz. per 10 gallons) before the addition of the colouring matter. The latter should be well dissolved, and may be added in one lot before dyeing. Most of the colours are dyed in feebly alkaline baths with some soda, soap, Turkey red oil or phosphate of soda, to which such neutral salts as common salt or Glaubersalt are added. The first-named products make the dyestuffs more soluble, whereas the neutral salts and also phosphate of soda promote the exhaustion of the dye-baths. The latter are generally used in quantities of 10 to 20 grms. (or even more) per litre; but should not be used in quantities large enough to precipitate the dyestuff, thereby producing irregular shades, and the dye-liquor should never exceed the specific gravity of 1.03 (6° Tw.). If a difficulty is experienced in levelling the colours, it is well to add the (neutral) salt in two portions, or after the material has been worked in the bath for about fifteen minutes, or to add some more Turkey-red oil or soap or soda to the bath. Sodium phosphate, which is used in quantities of about 10 grms. per litre, also improves the exhaustion of the dye-bath, but does not give rise to irregularities so easily as common salt or Glaubersalt. Colours which are sensitive to the action of alkalis are sometimes dyed in neutral baths, but this is not an important point, the alkali being easily removed by rinsing. Acid-baths are used in very rare cases only.\*

The dyed goods may be dried without washing. A light rinsing in water, however, is useful for diminishing the bleeding, and for preventing the efflorescence of Glaubersalt, &c. In the case of colours which are sensitive to acids, it is of great advantage to pass the material after dyeing through a solution of soda, which may contain as much as 5 parts of soda ash in 100 parts of water. Greater brilliancy is obtained by passing the goods through a solution of Turkey-red oil which has been neutralised with soda. In the case of colours which are sensitive to alkalis, the shade is sometimes brightened by weak acetic acid. Black colours are usually soaped in a tepid bath with the addition of a little olive oil to enhance the appearance of the

\* Recently a process has been patented by W. Warr for mordanting cotton with magnesium hydroxide before dyeing with direct cotton colours, by means of which it is possible to better exhaust the bath and to obtain colours which are faster to washing. British Patent, 1904, No. 25,165. *Journ. Soc. Dyers and Col.*, 1905, p. 118.

shades. *Mercerised cotton* is dyed with special care to avoid unevenness. Less salt is used, but the addition of soap or Turkey-red oil is increased whilst the temperature of the dye-bath is kept at 80° or less. Cotton which has been unevenly dried after mercerising will not dye evenly.

The process of diazotising and developing (see p. 380) is carried out in the following manner:—

The cotton is dyed with the dyestuff to be diazotised as described above for direct shades, and thoroughly washed in water to remove surface colour. The depth of the ultimate shade chiefly depends on the depth of the direct shade.

The dyed cotton is passed into the *cold* diazotising bath, which is prepared with 1½ to 3 per cent. sodium nitrite of the weight of the cotton, and twice the amount of sulphuric acid, or three times the amount of hydrochloric acid. Although the diazo-compound is formed instantaneously, the cotton is turned in this bath for about fifteen minutes to allow the diazotising liquor to penetrate the material entirely. The cotton is then rapidly rinsed in cold acidulated water, and immediately entered into the developing bath.

The nitrite bath may be used continuously; if it does not slightly smell of nitrous acid, or is not sufficiently acid, nitrite or sulphuric acid respectively is added; a moderate excess of either substance is not injurious.

The development should take place without unnecessary delay, for, like all diazo-compounds, these diazotised colours are unstable and begin to decompose within the first hour, or even immediately when exposed to the light or to a slightly elevated temperature. Thus a very short exposure to direct sunlight is liable to produce considerable unevenness, so as to spoil the goods.

The diazotised colour is manipulated in the cold developing bath, prepared with one or several of the various developers (see below). The new colour, which may appear similar in shade to the direct one, or be totally different, is developed at once, and the manipulation is only prolonged to allow the liquor to thoroughly penetrate the material. The bath must contain a sufficient quantity of the developer to saturate the whole amount of diazo-compound contained in the fibre. Unless the bath is in the right condition as to strength and alkalinity or acidity, the diazo-compound will not be thoroughly converted into the new colour, and will rapidly decompose; the new colour will therefore appear very sensitive to light, &c. The developing bath can also be used continuously if fresh developer is added as the bath becomes exhausted. After developing, the cotton is rinsed in water, and is then ready for further applications.

Mixed shades may be produced by either mixing several developers, or several diazotisable dyestuffs may be dyed together, or ordinary direct colours, which are not affected by the diazotising process, may be dyed together with the diazotisable dyestuff; or the diazotised colour may be topped with a basic dyestuff like the direct shades.

A very simple method of developing, which is recommended for the production of very fast brown shades with some dyestuffs, such as Diamine cutch and Diazo-brilliant black, consists in the *treatment of the diazotised colour in a warm solution of soda*. The dyed cotton is entered into the diazotising bath, as previously described, and then, without rinsing, turned for ten to twenty minutes in a bath heated to 50° or 60° C., containing 1½ to 2 grms. soda ash per litre; after a light rinsing the shade is ready.

**Developers.**—Of the developers which are phenols or amines or their sulphonic acids, the following are the most important:—

1. *Phenol* (or *Yellow developer*, developer J).—950 grms. cryst. phenol and 2,400 grms. caustic soda lye 1.375 specific gravity (75° Tw. = 34 per cent. NaOH) are dissolved in 20 litres of hot water.

2. *Resorcin* (or *Orange developer*, developer F).—1,100 grms. resorcinol and

2,400 grms. caustic soda lye 1.375 specific gravity are dissolved in 20 litres of hot water.

3a. *Beta-naphthol* (or *Red developer*, developer A).—1,450 grms.  $\beta$ -naphthol and 1,200 grms. caustic soda lye 1.375 specific gravity are dissolved in 20 litres of hot water.

3b. *Alpha-naphthol* (or *Maroon developer*) is used like  $\beta$ -naphthol.

4. *Meta-toluylene diamine* (or *Diamine developer C, E, or H*) is found in commerce as the hydrochloride in various forms; as powder of varying strengths (developers C or H) and in solution (developer E). Of the 95 per cent. powder 900 grms. are dissolved in 20 litres of boiling water. In order to prevent the formation of Bismarck brown, 50 grms. of soda ash per 20 lbs. of cotton are added to the bath together with the Diamine developer.

5. *Naphthylamine ether* or *Amidonaphthol ether* is sold as powder or paste; of the paste 1 kg. is simply dissolved in 10 litres of boiling water, whereas of the powder 460 grms. are dissolved together with 230 grms. of hydrochloric acid in 20 litres of boiling water.

6. *Amidodiphenylamine* (or *Fast blue developer A D*).—750 grms. are dissolved together with 350 grms. of hydrochloric acid in 20 litres of boiling water.

7. *Ethyl  $\beta$ -naphthylamine* (or *Claret developer*, developer B).—460 grms. are dissolved together with 100 grms. of hydrochloric acid in 20 litres of boiling water.

8. *Amidonaphtholsulphonic acid*, mixed with soda, or *Blue developer A N* or *developer G*.—2,700 grms. are mixed with 20 litres of cold water, and left standing until the frothing has subsided, when the mixture is brought to the boil.

9.  *$\beta$ -Naphtholsulphonic acid* or *Schaeffer acid*.—2,500 grms. are mixed with 1,500 grms. of soda ash, and dissolved in 20 litres of boiling water.

10. *Nerogene D* (Berlin), a chlorinated diamine, is used as follows:—90 grms. Nerogene D are dissolved in 300 grms. water and 90 grms. hydrochloric acid, and added, together with 300 grms. soda ash, to the bath for developing 10 kilos. of cotton.

Of the solutions named under Nos. 1, 2, 3, and 9, 1½ litres per 20 lbs. of cotton should be used for the first bath, and 1½ to 1½ litres of Nos. 4 and 8, 6½ litres of Nos. 5 and 7, and 4 litres of No. 4. The quantities required in the standing bath are approximately the same. The quantities actually used amount to about 1 per cent. naphthol, 0.7 per cent. diamine or resorcin, ½ per cent. phenol, 1½ per cent. naphthylamine ether or amidodiphenylamine, or Schaeffer acid, and 2 per cent. amidosulphonic acid. An excess of developers does no harm, if it is subsequently removed by rinsing.

The phenolic developers and also phenylene diamine, toluylene diamine, and Nerogene D are used in alkaline solutions, the other developers in neutral or acid solutions. The developers used in alkaline solutions may be mixed together for the production of mixed shades, and the developers to be used in acid solutions may also be mixed with each other. It may be noted, however, that when used in excess, one developer may have proportionately more effect than another.

The colours obtained by diazotising and developing may be topped with basic colours exactly as in the case of the direct dyed ones.

For the coupling process (see p. : 80) the cotton is dyed according to the general method, and after rinsing it is treated for about half an hour in the cold coupling bath prepared with the diazo-compound, including some soda and acetate of soda to neutralise the surplus of mineral acid.

The most important developer for coupling is paranitraniline, which is used in the following manner:—2 kilos. of paranitraniline are well mixed with 15 litres of boiling condensed water, and, after some stirring, 5 litres hydro-



chloric acid 1.16 specific gravity (32° Tw.) are added. The mixture will dissolve after some stirring, when 35 litres of cold water are added in order to precipitate the hydrochloride as a yellow pasty mass of fine crystals. After it has been thoroughly cooled either by being allowed to stand, or by the addition of ice, 1½ kilos. of sodium nitrite dissolved in 7 litres of cold water are added, and within fifteen or twenty minutes a clear solution will be obtained, which is diluted to 200 litres. For coupling medium shades (of 1½ to 2 per cent. colour) 36 litres of this diazo-solution, together with ½ kilo. soda ash and 200 grms. sodium acetate, are used per 100 kilos. of cotton; for deep shades 50 to 70 litres diazo-solution, ¾ to 1 kilo. soda ash, and 300 to 400 grms. sodium acetate are required. For coupling colours on loose cotton and for working in dyeing machines, the diazo-solution may be used without the addition of soda or acetate.

Instead of using diazotised paranitraniline, such stable diazo-compounds as Nitrazol C (Cassella) or Azophor red P N (M.L.B.) or Nitrosamine red (B.A.S.F.) may be employed. Other developers recommended for coupling are benzidine and mononitrobenzidine—i.e., developer NB (Basle).

The fastness to light of some coupling colours is increased by the addition of 2 to 4 per cent. blue vitriol to the coupling liquor.

The coupled colours may also be brightened by topping with basic colours, which may be effected by simply adding the basic colour to the coupling bath.

The after-treatment with metallic salts is best conducted in a bath slightly acidulated with acetic acid. An alkaline condition of the bath preventing the action of the salts, the cotton dyed with the addition of soda should be well rinsed preceding the after-treatment. The cotton should be entered at a moderate temperature into the bath of after-treatment, and well turned. The bath may be employed continuously, but with little advantage, on account of the low price of the drugs.

The various metal salts are used in the following way:—(a) *Copper sulphate*.—The goods are treated for fifteen to thirty minutes at 80° C. with 1 to 4 per cent. copper sulphate (according to the depth of shade) and 2 to 4 per cent. acetic acid. (b) *Chromium fluoride*.—The dyed cotton is boiled for a quarter to half an hour with 1 to 3 per cent. chromium fluoride and 2 to 4 per cent. acetic acid. Other salts of chromium oxide are used in the same way. (c) *Bichromate*.—The goods are boiled ten to fifteen minutes with 1 to 3 per cent. bichromate and 2 to 4 per cent. acetic acid. Some colours becoming lighter and duller by a prolonged action of the bichromate, the boiling should not be extended too long. (d) *Bichromate and Copper sulphate*.—The after-treatment is the same as with bichrome alone, one-half of the latter being replaced by blue vitriol. The after-treatment being finished, the cotton is well rinsed. The colours may also be topped with basic colours.

Some diazotised or coupled colours are improved in fastness to light by either after-treating with copper sulphate, as just described, or adding the copper salt directly to the cold diazotising or coupling bath.

The after-treatment with bichromate and copper sulphate may be very well combined with the production of *one-bath aniline black* on a bottom of a dark direct cotton colour by dyeing a fairly deep shade with a black or dark blue dyestuff, and then developing *one-bath aniline black*. In this way a finer black is obtained, and one faster to rubbing and acids and less disposed to becoming greenish than with aniline black alone, and the strength and softness of the fibre is preserved. In addition to such dyestuffs as Benzochrome black, Chromanil black or Diamineral black which are intended for the after-treatment with a mixture of bichrome and copper, such other dyestuffs may be used which are not affected by this mixture. This black is very fast and clean, and in many cases it may replace *aged aniline black*.

The treatment with formaldehyde, which improves the fastness to washing, takes place at 50° to 70° C., the dyed cotton, after rinsing, being simply turned for about fifteen minutes in a bath containing 3 to 4 per cent. formic aldehyde (40 per cent.).

A treatment with Solidogene A (M.L.B.) improves the fastness to washing and acids, and is especially recommended for Dianile orange G, Dianile scarlet G, 2 R, Dianile red R, 4 B, 6 B, 10 B, Dianile bordeaux B, G, Brilliant dianile red R, Delta purpurine 5 B, Dianile blue G, B, R, 2 R, 3 R, 4 R, BX, Dianile indigo O, Dianile dark blue R, Dianile black R, G, CB, CR, and for Primuline red. The dyed and rinsed cotton is boiled for half an hour with 2 per cent. hydrochloric acid and 2 to 6 per cent. Solidogene A, and then well rinsed. When the treatment takes place in copper vessels, 5 to 10 grms. ammonium sulphocyanide per 10 litres ( $\frac{1}{2}$  to 1 lb. per 100 galls.) should be added before the other additions.

The topping of direct cotton colours with basic colours for the purpose of brightening or shading the former is carried out by working the cotton well rinsed after dyeing in a cold bath containing the basic colour, and, in addition, 1 to 3 per cent. acetic acid or alum. Higher temperatures destroy the colour lake thus formed. The process is frequently used both with direct and with after-treated, diazotised or coupled colours.

Linen and Jute are dyed in practically the same way as cotton.

ARTIFICIAL SILK is also dyed like cotton at 30° to 60°, careful handling being necessary in order to prevent damaging the material, which is very tender in the wet state.

**DYEING OF WOOL WITH THE DIRECT COTTON COLOURS.**—The colours are dyed on wool in neutral or feebly acid-baths. For light shades the bath is simply prepared with the dyestuff, and the wool entered at 40°, the bath is brought to the boil, and after some boiling, 10 per cent. Glaubersalt are added for the better exhaustion of the bath. For medium and dark shades the Glaubersalt may be added before entering the wool, and after the colour has been fairly well taken up, 2 to 5 per cent. acetic acid or sodium bisulphate may be gradually added in order to exhaust the bath entirely; great care, however, is required that the colour does not become uneven on acidulating the bath. The dye-bath may also be prepared with Glaubersalt and 5 to 10 per cent. ammonium acetate (of the weight of the wool); the latter salt by splitting off ammonia on boiling liberates acetic acid, which effects a very gradual exhaustion of the dye-bath. (Care should be taken not to use an acetate containing excess of acetic acid.)

These colours are considerably faster to washing, acids, and light on wool than on cotton, and are also much faster to milling than most of the ordinary acid colours; indeed, fast enough for many kinds of goods to be milled. They are, as a rule, also fast to stoving, steaming, and alkalies.

Some colours are after-treated with metallic salts also on wool, especially with copper sulphate, but the diazotising or coupling processes are not generally used on this fibre.

*N.B.*—The shades on wool and also on silk frequently differ somewhat from those obtained on cotton.

**DYEING OF SILK WITH THE DIRECT COTTON COLOURS.**—Silk is best dyed in a bath containing  $\frac{1}{10}$  of its volume of boiled-off liquor, which is acidulated with acetic acid. Enter at about 50°, then boil, and exhaust the bath after three-quarters of an hour's boiling by adding 2 to 4 per cent. acetic acid or 2 to 3 per cent. sulphuric acid; finally rinse and brighten with acid.

The colours are about equal in fastness to those on wool, and are generally much faster to water than the ordinary acid colours.

The fastness to soaping is much improved by subjecting suitable colours to

the process of diazotising or coupling, or after-treating with bichrome or chromic salts; some colours will then stand the boiling-off.

These processes are carried out as on cotton. The quantity of bichrome used on silk, however, should not exceed  $1\frac{1}{2}$  per cent. of the weight of the silk, nor one-third of the colouring matter, and the developing with soda may with advantage be replaced by a five minutes' treatment with 5 per cent. sulphuric acid at  $70^{\circ}$  to  $80^{\circ}$ .

**DYEING OF UNION GOODS (COTTON AND WOOL MIXED GOODS) WITH DIRECT COTTON COLOURS.**—The direct cotton colours have acquired special importance for the dyeing of mixed goods by their property of dyeing cotton and wool in one bath, whereby the dyeing of such goods has been considerably simplified.\*

The dyeing of union goods with direct cotton colours in a single bath is based on their property of dyeing cotton about equally well at different temperatures, and wool much easier at higher than at lower ones. Hence, in order to dye goods consisting mainly of cotton, the material is turned without much heating, while the bath is brought to the boil for dyeing the wool. If, after some time, the cotton should be too light, dyeing is continued with the steam shut off. If, on the other hand, the wool should not be sufficiently covered, the bath is boiled, and, in addition, certain acid colours which dye wool well in a neutral bath are added.

*N.B.*—Although the dyeing of the wool might be accelerated by acidulating the bath, this, as a rule, should be avoided, as the cotton might come out too light. Care should also be taken not to use any Glaubersalt having an acid reaction, and to cleanse out with boiling soda any wooden dye-vats which have been previously used for acid dyeing. The following is the general mode of procedure for the one-bath method:—

Piece goods are best dyed on the winch, and yarns in the ordinary dye-vat or in dyeing machines. The bath is kept rather concentrated—that is, for dark shades the weight of the water is about 25 to 30 times that of the goods—and 20 to 40 grms. cryst. Glaubersalt are added per litre of dye-liquor. After the required cotton colours, and in case of sufficient experience the wool colours also, have been added, the bath is heated to the boil, the steam shut off, and the goods entered and dyed half an hour, and a sample then taken. If both fibres are found too light or off-shade, more colours are added, and after the bath has been brought to the boil, the steam is shut off again and the dyeing continued. If the wool only is too light or off-shade, the goods are dyed for a short time at the boil, with or without the addition of wool colours, as the case may be, some care being necessary not to dye the wool too intensely. If, however, the cotton only requires shading, cotton colours are added, and the dyeing is continued without heating. The dyeing being finished, the goods are rinsed, and may be subsequently brightened with a little acid ( $\frac{1}{2}$  gm. acetic or sulphuric acid per litre). Alkaline blue must be developed in an acid bath. After the treatment with sulphuric acid it is necessary to rinse well in order to remove the acid so as to prevent tendering of the cotton fibre. The risk of tendering is avoided by the addition of 3 to 5 grms. sodium acetate per litre (5 to 8 ozs. per gallon) to the acid-bath or last rinsing bath.

With some goods which contain many knots of cotton on the surface, or which are made from hard twisted yarns, it is better first to dye the wool in an acid-bath, and after it has been nearly brought to shade to dye the cotton in a dolly in a very concentrated cold or tepid bath containing 20 grms. Glaubersalt and  $\frac{1}{2}$  gm. soda ash, or better, 2 grms. ammonia per litre, dyestuffs being preferred for this method which dye chiefly the cotton without

\* The process of dyeing mixed goods in a single bath was devised by L. Cassella & Co. in the early nineties of the last century.

staining the wool very much. This method may also be used for the production of two-coloured effects in the piece.

**DYEING OF SATINS (COTTON AND SILK MIXED GOODS) WITH DIRECT COTTON COLOURS.**—The direct cotton colours are equally applicable to cotton and wool mixed goods and to those consisting of cotton and silk, and the same process may be used. In the case of half-silk goods, however, the dyeing is usually begun in a fairly alkaline bath so as to dye principally the cotton, and either the silk alone or both fibres together are afterwards brought to shade with acid or basic dyestuffs.

Light shades are dyed with the addition of 200 to 400 grms. soap and 15 to 25 grms. soda ash, and sometimes 200 to 400 grms. sodium phosphate also, per 100 litres of liquors; for medium and dark shades, in addition to these drugs 400 to 800 grms. Glaubersalt are given to the bath. The bath is boiled up, and the goods are then dyed without heating for three-quarters to one hour. In the case of light shades the material is usually entered at a lower temperature in order to avoid unevenness, and the bath is gradually heated. The higher the temperature the darker the silk is coloured.

The dyeing to shade is usually done in a cold or tepid bath with acid or basic colours with the addition of sulphuric or acetic acid, acid dyestuffs being used for dyeing the silk only, whereas basic colours serve for both fibres.

For the production of two-coloured effects the quantity of soap is increased to 300 to 500 grms. per 100 litres, and such dyestuffs are used as dye the cotton and leave the silk entirely or nearly white. After the cotton has been dyed, the material is well rinsed and dyed at 50° C. with acid dyestuffs with the addition of 2 grms. sulphuric acid per litre. A higher temperature or a greater amount of acid should be avoided in order to prevent the cotton colours staining the silk. Finally the pieces are well rinsed, and brightened with 2 to 4 c.c. acetic acid per litre.

**CONGO-RED** (Berlin, Bayer, Leonhardt, Levinstein). **CONGO-RED R.**  
**COTTON RED.** **COSMOS RED.**

Benzidine < naphthionic acid.  
naphthionic acid.

Red-brown powder; aqueous solution, orange-red; HCl, blue precipitate; \* NaOH, no change; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, blue precipitate. Congo-red is so extremely sensitive to acids that it is used as an indicator for volumetric analysis.

*Application.*—See also general remarks (pp. 381, *et seq.*). Calcareous and magnesian water must be avoided or purified. Congo-red, on account of the richness of its shade and its low cost, is still used in great quantities for cotton dyeing, but to a small extent only on wool or silk.

**Cotton.**—For a full shade boil one hour in a concentrated bath with 3 to 4 per cent. of Congo-red, 20 per cent. of Glaubersalt, and 5 per cent. of soda ash. After dyeing, pass through a solution of soda (containing 2 to 5 parts of soda ash in 100 of water), wring and dry. The brilliancy is increased by passing the dyed goods through Turkey-red oil which has been neutralised with soda; if the goods are to be finished, the oil may be added to the finishing material. The following methods have also been recommended:—Boil for 1½ hours in a bath containing the required amount of dyestuff—3 per cent. of aluminate of soda, 3 to 5 per cent. of soap, and 10 per cent. of Turkey-red oil, allow to cool in the bath, wring, and dry. Or boil for two hours with the necessary amount of dyestuff—3 per cent. of stannate of soda and 4 per cent. of soft soap, allow to cool in the bath overnight, wring, and dry. Cotton can also be mordanted

\* The blue precipitate does not represent the free colour acid, but consists of an unstable hydrochloride, which is decomposed by prolonged washing with distilled water.

either with Turkey-red oil and alumina or with stannate of soda or with magnesium hydrate (Warr's process, p. 381), and then be dyed in a second bath with Congo-red. These methods yield richer shades than the one first described.

Congo-red dyes a bright scarlet-red approaching the shade of Turkey-red, but it does not compare with this colour in fastness to washing, and it is very sensitive to air and light and to acids. A short exposure of goods dyed with Congo-red to the air and light dulls the colour; but it will be brightened again by soaping. By continued exposure the shades are thoroughly bleached in a short time. Goods dyed with Congo-red are extremely sensitive to the action of acids, being turned blue; even the sulphurous acid contained in the air has a dulling effect. The treatment of the dyed goods with soda or soap solution, and even with neutralised Turkey-red oil, lessens the sensitiveness to acids and makes the colour a little faster to light.

Wool and Silk are dyed with Congo-red in a boiling bath containing neutral salts, to which some soap or soda or phosphate of soda may be added. Deeper, but less brilliant shades, are obtained by dyeing at the boil in a slightly acidulated bath, and subsequently passing through a weak solution of soda. Congo-red, although it is much faster to light and acids on the animal fibres than on cotton, is not used very frequently on the former on account of its sensitiveness to acids. The colour may be considered to be very fast to milling.

Mixed Goods are dyed with Congo-red, as described on pp. 386 and 387.

**CONGO-RED G R** and **4 R** are similar to Congo-red in constitution and properties.

**BRILLIANT CONGO G** (Berlin, Bayer, Leonhardt, Levinstein).

Benzidine  $\left\{ \begin{array}{l} \text{betanaphthylamine disulphonic acid R.} \\ \text{betanaphthylamine monosulphonic acid Br.} \end{array} \right.$

Brown-red powder; aqueous solution, orange-red; HCl, dark red-violet precipitate; NaOH, no change; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, violet precipitate.

*Application and Properties.*—Same as Congo-red; the shade is brighter and yellower, and less sensitive to acids.

**BRILLIANT CONGO R** is very similar in constitution and reactions to Brilliant Congo G, being the corresponding tolidine-compound. The shade resembles ordinary Congo-red, but it is more brilliant and less sensitive to acids.

**BENZOPURPURIN 4 B** (Bayer, Berlin, Leonhardt, Levinstein). **DIAMINE RED 4 B**. **DIANILE RED 4 B**. **COTTON RED 4 B**. **SULTAN 4 B**.

Tolidine  $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{naphthionic acid.} \end{array} \right.$

Brown-red powder; aqueous solution, orange-red; HCl, blue precipitate; NaOH, soluble orange-red precipitate; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, blue precipitate.

*Application and Properties.*—Same as Congo-red; the shade is nearly the same, but less intense. It is less sensitive to acids, and about equal in fastness to light and washing. Benzopurpurine 4 B is one of the most important of the direct colours, and is frequently used for wool dyeing also.

**BENZOPURPURIN B** and **6 B** are similar to the 4 B brand in application and properties, Benzopurpurin B dyeing yellower shades and 6 B bluer shades than 4 B. Benzopurpurin B is slightly faster to acids than 4 B.

**BENZOPURPURIN 10 B**. **SULTAN 10 B**.

Dianisidine  $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{naphthionic acid} \end{array} \right.$

Brown powder; aqueous solution, scarlet-red; HCl, blue precipitate; NaOH, soluble red precipitate; solution in  $H_2SO_4$ , blue; on diluting, blue precipitate.

*Application and Properties.*—Benzopurpurin 10 B dyes a crimson-red shade like Benzopurpurin 4 B.

**BRILLIANT PURPURIN R** (Berlin, Bayer, Leonhardt, Levinstein).

Tolidine < betanaphthylamine disulphonic acid R.  
naphthionic acid.

Brownish-red powder; aqueous solution, claret-red; HCl, black precipitate; NaOH, soluble red precipitate; solution in  $H_2SO_4$ , violet-blue; on diluting, black precipitate.

*Application and Properties.*—Brilliant purpurin R shows the same properties as the Benzopurpurins, and is dyed like these by the same methods as Congo-red. It is, however, somewhat faster to light and acids than the preceding dyestuffs. It yields brilliant shades which are slightly bluer than Congo-red and Benzopurpurin 4 B.

**BRILLIANT PURPURIN 10 B** (Berlin) is similar, but dyes bluish-red shades.

**DELTA PURPURIN 5 B** (Bayer, Berlin, Leonhardt, Levinstein). **COTTON PURPURIN 5 B** (B.A.S.F.).

Tolidine < betanaphthylamine deltamonosulphonic acid.  
betanaphthylamine monosulphonic acid Br.

Brown-red powder. Aqueous solution, orange-red; HCl, red-brown precipitate; NaOH, soluble orange-red precipitate; solution in  $H_2SO_4$ , blue; on diluting, red-brown precipitate.

*Application.*—Same as Benzopurpurin. It dyes a red shade similar to that of Benzopurpurin 4 B, but less bright and faster to acids.

**DELTA PURPURIN 7 B** is very similar to the "5 B" brand and dyes slightly bluer shades of red.

**COLUMBIA FAST SCARLET 4 B** (Berlin).

Brown-red powder; aqueous solution, orange-red; HCl, makes the solution more orange and produces a brownish precipitate; NaOH, orange-red solution and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, brownish precipitate.

*Application.*—Same as Benzopurpurin. Columbia fast scarlet 4 B is best dyed on cotton, at about  $70^\circ C.$ , with the addition of 40 per cent. Glaubersalt and 1 per cent. soda ash. Its shade is very bright, and slightly bluer than that of Benzopurpurin 4 B, and distinguished by its very good fastness to organic acids; it is also very fast to alkalies, but not very fast to washing, and it is fugitive to light. On wool it is dyed in a bath acidulated with acetic acid.

**CONGO RUBIN** (Berlin, Levinstein). **COTTON RUBIN** (B.A.S.F.).

Benzidine <  $\beta$ -naphthol monosulphonic acid B.  
naphthionic acid.

Green crystalline powder; aqueous solution, cherry-red; HCl, blue precipitate; NaOH, soluble violet-brown precipitate; solution in  $H_2SO_4$ , blue; on diluting, blue precipitate.

*Application and Properties.*—Same as Congo-red. Congo rubin yields a fine bluish-red (ruby-red or claret) shades.

**COLUMBIA RED 8 B** (Berlin).

Brown powder; aqueous solution, magenta-red; HCl, red precipitate;

NaOH, more bluish-red solution and soluble violet-red precipitate; solution in  $H_2SO_4$ , red; on diluting, at first violet-red solution, then red precipitate.

*Application.*—Same as Congo-red and Benzopurpurin. Columbia red 8 B on cotton yields pink and full bluish-red shades which are distinguished by fastness to acids.

**BENZO FAST RED L** (Bayer).

Brown powder; aqueous solution, red; HCl, violet-blue precipitate; NaOH, orange-red solution and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet-blue precipitate.

*Application.*—Same as Benzopurpurin. It dyes on cotton a somewhat bluer and less bright shade, which is fairly fast to light, washing, acids, and alkalis. The dyestuff may also be used with advantage on wool and silk and on mixed goods. The shades on wool are fairly fast to milling and very fast to light, and on silk very fast to light and washing.

**BENZO FAST RED G L** (Bayer) is similar to the preceding "L" brand. It is more yellowish in shade, and superior in fastness to acids.

**BENZO RHODULIN RED B and 3 B** (Bayer).

*Benzo rhodulin red B.*—Light brown powder; aqueous solution, red; HCl, bluish-red solution and flocculent precipitate; solution in  $H_2SO_4$ , orange-brown; on diluting, bluish-red and flocculent precipitate.

*Benzo rhodulin red 3 B* shows similar reactions.

*Application.*—Same as Benzopurpurin. The two brands are dyed on cotton with 10 per cent. sodium sulphate and  $\frac{1}{2}$  per cent. soda ash. They yield pink or bluish-red shades, which are fast to acids and alkalis and fairly fast to washing, but not fast to light.

**BENZO BORDEAUX 6 B** (Bayer).

Brown powder; aqueous solution, bluish-red; HCl, red precipitate; NaOH, makes the solution more yellowish; solution in  $H_2SO_4$ , greenish-blue; on diluting, red precipitate.

*Application and Properties.*—Same as Benzo rhodulin red (see above). It dyes pink and cardinal red shades, which are still bluer than those of Congo rubin.

**BENZO FAST SCARLET 4 B S** (Bayer).

For the production of the various brands of Benzo fast scarlet and Benzo orange S the urea obtained by the action of phosgene gas upon 2 molecules of amidonaphthol sulphonic acid J ( $NH_2 : OH : SO_3H = 1 : 5 : 7$ ) is combined with 2 molecules of diazo-compounds.

Red-brown powder; aqueous solution, orange-red; HCl, reddish-brown precipitate; NaOH, soluble brown-red precipitate; solution in  $H_2SO_4$ , blue-violet; on diluting, reddish-brown precipitate.

*Application.*—Same as Congo-red. Benzo fast scarlet 4 B S is similar in shade to Benzopurpurin 4 B, and equals the same in fastness to washing, whilst it is somewhat faster to light, and greatly superior in fastness to acids. It stands the action of organic acids and dilute mineral acids very well, and for the latter reason it is also useful for the dyeing of cotton in satins which are cross-dyed in an acid bath. It may also be used with advantage for dyeing unions by the one-bath method.

**BENZO FAST SCARLET 5 B S and 8 B S** dye brighter and bluer shades of red, whereas

**BENZO FAST SCARLET G S** dyes deeper orange shades than 4 B S.

*Application and Properties.*—Same as Benzo fast scarlet 4 B S.

**DIAMINE-SCARLET B** (Cassella).

Benzidine  $\left\{ \begin{array}{l} \text{betanaphthol gammadisulphonic acid.} \\ \text{phenetol.} \end{array} \right.$

This dyestuff is produced by combining tetrazoditoyl with the sulphonic acid and phenol, and ethylating the azo-compound.

Red powder; solution, scarlet-red; HCl, reddish-brown precipitate; NaOH, makes the solution more yellowish; solution in  $H_2SO_4$ , blue-violet; on diluting, reddish-brown precipitate.

*Application*—Cotton.—Diamine-scarlet B is dyed in the same way as Congo red; it dyes a bright scarlet shade which is not sensitive to dilute acids and not fast to light.

Wool is dyed with Diamine-scarlet B in a boiling neutral bath with the addition of sodium sulphate; the bath may be cautiously exhausted by the addition of 2 to 5 per cent. acetic acid. The shade on wool is very bright, and excellent in fastness to light; also very good to washing and milling.

Silk is dyed in an acidulated bath of boiled-off liquor or with the addition of acid very fast to light and to the water test, also to acids and alkalies.

**DIAMINE SCARLET 3 B** (Cassella) is similar to the B brand but more bluish in shade.

**DIAMINE BRILLIANT SCARLET S** (Cassella) also resembles Diamine scarlet B, but is still faster to acids.

**DIAMINE FAST RED F** (Cassella).

Benzidine  $\left\{ \begin{array}{l} \text{gamma-amidonaphthol sulphonic acid} \\ \text{(combined in acid solution).} \\ \text{salicylic acid.} \end{array} \right.$

Red-brown powder; aqueous solution, claret-red; HCl, brown-red precipitate; NaOH, soluble red-brown precipitate; solution in  $H_2SO_4$ , purplish; on diluting, brown-red precipitate.

*Application*.—Cotton is dyed as with Congo-red, either with 15 per cent. of calcined (35 per cent. of crystallised) Glaubersalt and 5 per cent. of soda ash or by the other methods.

Diamine fast red F dyes a shade of red similar to Benzopurpurin 4 B and Congo-red, but not so bright; it is not sensitive to dilute acids, and is fairly fast to light.

Wool is dyed in a neutral or slightly acid-bath; the shade is very fast to milling and stoving, as also to light. The fastness to milling becomes still better if the goods are boiled after the bath is exhausted with some acetic acid for half an hour longer, with the addition of chromium fluoride, or, for dark shades of bichrome to the old dye-bath; 1 to 3 per cent. of chromium fluoride or 2 to 3 per cent. of bichrome are required. The shades thus obtained rival madder-red in fastness to light and milling. This dyestuff is also to be recommended for topping vat-blues.

Silk is dyed in a bath which has been acidulated with acetic acid, fast to light and to the water test, also to acids and alkalies.

**DIAMINE RED 10 B** (Cassella).

Brown powder; aqueous solution, claret-red; HCl, violet-black precipitate; NaOH, soluble pink precipitate; solution in  $H_2SO_4$ , blue; on diluting, dark precipitate.

*Application*.—Diamine red 10 B is dyed on cotton, unions, and satins in neutral or slightly alkaline baths, and yields a bright bluish-red of moderate fastness to washing; the shade is not fast to light; it resists the action of alkalies, but is turned blue by acids.

**DIAMINE RED 6 B** is a similar brand, yielding more yellowish shades of red.

**DIAMINE VIOLET RED** (Cassella) behaves similar to Diamine red 10 B in dyeing, but gives more bluish-red shades.



**DIAMINE BORDEAUX B and S (Cassella).**

Dark-brown powder; aqueous solution, claret-red; HCl, dark violet precipitate; NaOH, soluble dark red precipitate; solution in  $H_2SO_4$ , blue; on diluting, claret-red precipitate.

*Application.*—Cotton is dyed by the usual method with the addition of soda and sodium sulphate. Diamine bordeaux B yields a full bright claret-red which is fairly fast to light, washing, and alkalis, and is turned blue by acids. The "S" brand is less bright, and inferior in fastness to washing and light, but good to acids and alkalis.

Wool and Silk are dyed with Diamine bordeaux S in a neutral bath or in one slightly acidulated with acetic acid. A full claret is obtained which is very fast to milling, stoving, and light.

Unions and Satins are dyed with both brands by the one-bath system, Diamine bordeaux B being of special value for mixed goods.

**DIAMINE BRILLIANT BORDEAUX R (Cassella).**

Maroon-coloured powder; aqueous solution, claret-red; HCl, dark blue precipitate; NaOH makes the solution more yellowish; solution in  $H_2SO_4$ , dark blue; on diluting, dark blue precipitate.

*Application and Properties.*—Same as Diamine bordeaux B, except that Diamine brilliant bordeaux R possesses good fastness to dilute acids, its shade being hardly affected by acetic acid 50 per cent.

**DIRECT SCARLET G, R, B (Kalle).**

*Direct scarlet G.*—Brown powder; aqueous solution, magenta-red; HCl, violet-red precipitate; NaOH, no change; solution in  $H_2SO_4$ , violet-red; on diluting, violet-red precipitate.

*Application.*—Direct scarlet is dyed on cotton in a neutral or weakly alkaline bath with the addition of salt and soda, and yields handsome pink and bluish shades of very good fastness to acids, and fairly good fastness to washing and alkalis, but fugitive to light.

Dyestuffs of a similar character are—

**THIAMINE RED** (Sandoz).

**THIORUBIN** (Dahl).

**THIAZINE RED** (B.A.S.F.).

**TITAN SCARLET** and **TITAN RED** (Holliday).

**BENZO SCARLET S G** (Bayer).

**OXYDIAMINE RED S** (Cassella).

**DIOXYRUBIN B and G** (Basle Chemical Co.).

**THIAZINE RED G and R** (B.A.S.F.).

*Thiazine Red R.*—Brown powder; aqueous solution, magenta-red; HCl, violet-red precipitate; NaOH, no change; solution in  $H_2SO_4$ , magenta-red; on diluting, violet-red precipitate.

*Application.*—Thiazine red is used on cotton especially for light shades, and is dyed in a boiling bath with the addition of salt. Thiazine red R yields bluish-pinks and reds, and the "G" brand more yellowish shades of red which are very fast to acids and fairly fast to soaping and alkalis, but fugitive to light.

**OXAMINE RED** (B.A.S.F.).

Brown powder; aqueous solution, orange-brown; HCl, brown-red precipitate; NaOH, red solution and soluble red precipitate; solution in  $H_2SO_4$ , blue-violet; on diluting, brown-red precipitate.

*Application.*—Oxamine red is dyed on cotton with the addition of Glaubersalt, and yields full reds which are moderately fast to light, fairly fast to washing, and very fast to acids and alkalis.

**OXAMINE BORDEAUX M** (B.A.S.F.) is similar, and dyes claret shades.

**OXAMINE FAST RED F** (B.A.S.F.).—This dyestuff is identical with Diamine fast red F. It is applied in the same manner, and yields shades of the same fastness.

**TITAN SCARLET C, C B, D, and S (Holliday).**

*Titan Scarlet C and C B.*—Brown powder; aqueous solution, orange-red; HCl, soluble yellow precipitate; NaOH, darker solution; solution in  $H_2SO_4$ , crimson; on diluting, yellower.

*Titan Scarlet D and S* show similar reactions.

*Application.*—The various Titan scarlets are dyed on cotton in neutral or slightly alkaline baths with the addition of common salt or Glauber salt, and yield bright scarlet shades which are fairly fast to washing and fast to acids and alkalies.

Wool is dyed in a neutral bath or with the addition of acetic acid; the shades are very fast to milling and fairly fast to light.

Silk is dyed fast to water in a bath acidulated with acetic acid.

**BRILLIANT TITAN SCARLET Y (Holliday).**

Brown-red powder; aqueous solution, orange; HCl, no change; NaOH, makes the solution duller; solution in  $H_2SO_4$ , magenta; on diluting, yellower.

*Application.*—Same as Titan scarlet. Brilliant Titan scarlet yields bright orange-scarlet shades.

**TITAN RED S and 6 B (Holliday).**

Brown-red powder; aqueous solution, magenta-red; HCl, yellowish-red precipitate (S) or violet-red precipitate (6 B); NaOH, darker; solution in  $H_2SO_4$ , crimson; on diluting, red precipitate.

*Application and Properties.*—Same as Titan scarlet. Titan red 6 B may also be applied in the same manner as St. Denis red.

**DIANOL BRILLIANT RED R (Levinstein).** **TOLUYLENE RED (Oehler),**  
**CHLORANTINE RED 8 B (Chem. Ind. Basle).** **ACETO-PURPURIN (Berlin).**  
**DIPHENYL RED 8 B (Geigy).**

Orthochlorbenzidine  $\left\{ \begin{array}{l} \text{amido R salt.} \\ \text{amido R salt.} \end{array} \right.$

Violet-brown powder; aqueous solution, magenta-red; HCl, solution darker and soluble red precipitate; NaOH, yellower solution and soluble red precipitate; solution in  $H_2SO_4$ , blue; on diluting, red solution and red precipitate.

*Application and Properties.*—This dyestuff is dyed on cotton in a neutral or slightly alkaline bath with the addition of common salt or Glauber salt and some soap or soda, and yields a very brilliant bluish-red of excellent fastness to acids and fairly good fastness to washing, alkalies, and chlorine, but fugitive to light.

**HESSIAN PURPLE N, B, B EXTRA, and D (Leonhardt).**

Tetrazocompounds of diamidostilbene disulphonic acid.

*Hessian Purple N.*—Brown-red powder; aqueous solution, cherry-red; HCl, dark blue precipitate; NaOH, soluble crimson-red precipitate; solution in  $H_2SO_4$ , blue; on diluting, blue-black precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath. The four brands dye slightly bluish shades of red, fairly fast to washing, and to alkalies, but not fast to light or acids. Unions may be dyed by the general methods (p. 386).

**HESSIAN BRILLIANT PURPLE (Leonhardt, Berlin, Bayer).**

Red-brown powder; aqueous solution, orange-red; HCl, black precipitate; NaOH, soluble red precipitate; solution in  $H_2SO_4$ , violet; on diluting, blue-black precipitate.

*Application.*—Hessian brilliant purple is very similar to the preceding dyestuffs, but somewhat sensitive to alkalies. Cotton is dyed in a neutral salt bath. Hessian brilliant purple dyes a brighter shade than the other "Hessian purples."

**HESSIAN FAST RUBY** (Leonhardt).

Dark greenish-brown powder; aqueous solution, dark claret-red; HCl, dark brown precipitate; NaOH, makes the solution more yellowish; solution in  $H_2SO_4$ , dark blue; on diluting, dark brown precipitate.

*Application.*—Hessian Fast Ruby is dyed on cotton like Hessian purple N, and yields maroons of moderate fastness to soap, alkalies, and acids, and little fastness to light.

**DIRECT BORDEAUX B** (Leonhardt).

Brown powder; aqueous solution, claret-red; HCl, dark precipitate; NaOH, soluble claret-red precipitate; solution in  $H_2SO_4$ , blue; on diluting, dark precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath a very good claret shade, fairly fast to light and washing, good to alkalies, but sensitive to acids.

Wool and silk are dyed in neutral or slightly acid baths very fast to light, washing, milling, and stoving. Unions and satins are dyed with advantage by the ne-bath methods.

**CONGO-CORINTH G and B** (Berlin, Bayer, Leonhardt, Levinstein).  
**COTTON CORINTH G and B. DIANILE BORDEAUX G and B.**

Dark olive-green powder (G) or greenish-black powder (B); aqueous solution, bluish-red; HCl, reddish-blue precipitate; NaOH, soluble crimson precipitate; solution in  $H_2SO_4$ , blue; on diluting, reddish-blue precipitate.

*Application and Properties.*—Congo-corinth G and B are similar to Congo-red, and are dyed in the same way. They yield maroon shades, "B" dyeing the bluer shades.

**DIANILE SCARLET 2 R** (M.L.B.).

Red powder; aqueous solution, scarlet; HCl, brown precipitate; NaOH, yellow solution; solution in  $H_2SO_4$ , bluish-violet; on diluting, brown precipitate.

*Application.*—Cotton is dyed a bright scarlet moderately fast to washing, but not to light, and fast to acids and alkalies. By a treatment with Solidogene A the shade becomes more yellowish and faster to washing. Unions and satins may be dyed by the one-bath methods, the animal fibre being dyed rather deeper than the cotton.

Wool and silk are dyed fast to light and washing in acid-baths.

**DIANILE GARNET G and B** (M.L.B.).

*Dianile Garnet G.*—Brown powder; aqueous solution, claret-red; HCl, blue-black precipitate; NaOH, soluble brown-red precipitate; solution in  $H_2SO_4$ , greenish-blue; on diluting, at first greenish-blue, then violet-blue, and finally blue-black precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath garnet and claret-red shades which are moderately fast to light and washing, and good to alkalies, but sensitive to acids. The "B" brand dyes more bluish shades than the "G" brand, which is slightly faster to light. Unions and satins are dyed solid shades by the one-bath methods.

**ALKALI RED R** (Dahl).

Red powder; aqueous solution, red; HCl, brown precipitate; NaOH, darker solution and soluble precipitate; solution in  $H_2SO_4$ , violet; on diluting, brown precipitate.

*Application.*—Alkali red R dyes on cotton in a feebly alkaline salt bath a bright scarlet, fairly fast to washing, and good to alkalies, but not fast to light or acids. Unions and satins may be dyed by the one-bath methods.

**ALKALI GARNET** (Dahl).

Violet-brown powder; aqueous solution, garnet red; HCl, little change, and soluble precipitate; NaOH, more yellowish solution and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, brown-violet precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath a handsome garnet red, fairly fast to washing, acids, and alkalies, but not to light. Unions and satins may be dyed by the one-bath methods.

**TRIAZOL RED 6 B and 10 B (Oehler-Griesheim).**

Corinth-coloured powder; aqueous solution, claret-red; HCl, brownish precipitate; NaOH, soluble red to red-violet precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, blue-violet to blue; on diluting, brownish precipitate.

*Application.*—Triazol red is dyed on cotton in a feebly alkaline salt bath, and yields bluish-red shades, fairly fast to washing, good to alkalies, but not very fast to light or acids.

**TRIAZOL FAST RED B (Oehler-Griesheim)** dyes slightly more yellowish shades, and faster to light and acids than Triazol red 6 B, in other respects similar to this brand.

**SALMON-RED (B.A.S.F.).**

For the production of this dyestuff, para-amidoacetanilide is diazotised and combined with naphthionic acid, the acetyl group eliminated, and the product subjected to the action of phosgene gas (COCl<sub>2</sub>).

Dark flesh-coloured powder; aqueous solution, orange-yellow; HCl, reddish-blue precipitate; NaOH, soluble orange-yellow precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, magenta-red; on diluting, blue precipitate.

*Application.*—Salmon-red is applied in the same way as Congo-red, and possesses the general character of the colours of this group. It yields flesh-coloured to brown-orange shades, which are not fast to light, and are affected by dilute acids; in fastness to washing it also resembles Congo-red, &c.

**SALMON-RED (Berlin).**

Dehydrometaxylylidine—betanaphthylamine disulphonic acid R.

*Application and Properties.*—Similar to the following "Erika"  $\frac{1}{10}$  to  $\frac{1}{4}$  per cent. of dyestuff yield fine salmon coloured shades on cotton.

**ERIKA G (Berlin, Levinstein).**

Dehydrothiometaxylylidine—betanaphthol gammadisulphonic acid.

**ERIKA B (Berlin, Levinstein).**

Dehydrothiometaxylylidine—alphanaphthol epsilondisulphonic acid.

These two dyestuffs are, unlike the preceding, not tetrazo-compounds, but simple azo-compounds. They are produced by the action of the diazo-compounds of dehydrothioxylylidine, a monacid base, on naphthosulphonic acids.

Erika B and G show the same general reactions. Reddish-brown powder; aqueous solution, claret-red; HCl, red precipitate; NaOH, soluble crimson precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, red-violet; on diluting, orange-red precipitate.

*Application.*—Cotton is dyed by the usual method in a neutral or slightly alkaline bath.

Erika dyes pink shades which are fairly fast to light and not sensitive to a 5 per cent. solution of acetic acid; by less diluted hydrochloric acid the shade is turned yellowish. Erika shows also satisfactory fastness to washing. Erika B dyes a bluish-pink of great beauty; 1 per cent. of dyestuff gives a full pink. Erika G yields pleasing yellowish-pink shades. Unions and satins are well dyed by the one-bath methods.

The following dyestuffs possess very similar properties, and yield very similar shades:—

**BRILLIANT GERANIN B and 3 B (Bayer).**

**GERANIN G and BB (Bayer).**

**DIAMINE ROSE B EXTRA, B D and G D (Cassella).**

**TITAN PINK 3 B (Holliday).**

**ROSOPHENIN-GERANIN (Clayton).**

**DIRECT-ROSE (Basle Chemical Co.).**

**ST. DENIS RED** (Poirrier). **DIANTHINE**. **PATENT ROCK SCARLET** (Claus & Co.). **ROSOPHENINE 4 B** (Clayton). **TRONA RED 3 B** (Bayer). **COTTON RED S** (B.A.S.F.).

Diamidoazoxytoluene  $\left\{ \begin{array}{l} \text{alphanaphthol sulphonic acid N.W.} \\ \text{alphanaphthol sulphonic acid N.W.} \end{array} \right.$

Red-brown powder; sparingly soluble in water; aqueous solution, orange-red; HCl, red precipitate; NaOH, soluble orange-red precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, cherry-red; on diluting, red precipitate.

St. Denis red is different from the benzidine colours in being a tetrazo-compound of the diacid base, diamidoazoxytoluene, C<sub>14</sub>H<sub>12</sub>ON<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>. It is not taken up by the fibre as readily as the benzidine colours, and is dyed in a peculiar manner.

*Application.*—For 10 kgs. (10 lbs.) of cotton dissolve 200 to 300 grms. (3 to 5 ozs.) of St. Denis red in 6 litres (3 quarts) of water, in which have been dissolved 250 grms. (4 ozs.) of solid caustic soda, and heat; when all is dissolved add the solution to a dye-bath prepared with 200 litres (20 galls.) of water, 48 kgs. (48 lbs.) of rock salt, and a solution of 1,750 grms. (3½ lbs.) of solid caustic soda in 5 litres (½ gall.) of water. It is essential that this bath be kept constantly at a specific gravity of 21½° to 23° Tw. (measured at the elevated temperature of the bath). Heat the bath to 85° C., enter the cotton, heat up to 95°, and dye during 30 minutes at this temperature; the full depth of shade is not obtained if the temperature remains below 93°, and the results are the better the nearer the bath is heated to about 98°; but the bath must not be brought to actual boiling. (N.B.—The boiling point of the dye-liquor (if heated by steam coil) is considerably above 100°, on account of the large quantity of salt it contains.) After dyeing, pass the goods without rinsing through a 1 per cent. solution of sulphuric or hydrochloric acid, rinse well in cold water, wring, and dry. St. Denis red yields by this method a brilliant Turkey-red shade, which is fast to acids, but is turned yellowish by alkalis. St. Denis red does not bleed as much as the preceding colours when simply rinsed in water; but on being washed with white goods it colours them; it resembles the benzidine colours in fastness to soaping, and, like the majority of these, it is not fast to light.

**ROSOPHENINE 5 B, 6 B, and 10 B.** **TRONA RED 7 B and G G** are similar in reaction, application, and properties to the preceding dyestuff.

The three Rosophenines yield more bluish shades, whilst Trona red G G dyes an orange-red shade.

**ROSANTHRENE O, R, A, B, C B** (Ch. Ind. Basle).

*Rosanthrene A.*—Bright-red powder, not very freely soluble in water; aqueous solution, red; HCl, gelatinous red precipitate; NaOH, makes the solution darker and more yellowish; solution in H<sub>2</sub>SO<sub>4</sub>, crimson-red; on diluting, gelatinous red precipitate.

*Application.*—The Rosanthrenes belong to the group of diazotisable dyestuffs. They are dyed on cotton and diazotised and developed with β-naphthol like the other diazotisable dyestuffs, and yield very fine and brilliant orange, scarlet, and claret shades which are very fast to washing, alkalis, and acids, but not to light. They resemble Primuline-red in fastness, but are much brighter in shade. The direct shades are of no special value.

Rosanthrene O diazotised and developed with β-naphthol dyes a bright orange shade, the "R" brand a brilliant scarlet, "A" and "B" full reds, and "C B" a deep claret colour, which are easily discharged by reducing agents.

**ROSANTHRENE BORDEAUX B** (Ch. Ind. Basle) is similar to the preceding brands, and yields, when developed with β-naphthol, claret shades.

**DIAZO-BRILLIANT SCARLET G, B, 3 B, and 6 F, EXTRA (Bayer).**

*Diazo-brilliant Scarlet B Extra.*—Cinnamon-brown powder; aqueous solution, red; HCl, red precipitate; NaOH, difficultly soluble red precipitate; solution in  $H_2SO_4$ , dark cherry-red; on diluting, red precipitate.

*Application and Properties.*—These are also diazotisable dyestuffs which are dyed and developed in the usual way, and yield very fine and brilliant scarlet shades. The "G" brand dyes the most yellowish and "6 B" the bluest shades. They also resemble Primuline-red in fastness, but are much more brilliant.

**DIAZO-BORDEAUX (Bayer).**

Yellowish-green powder; aqueous solution, brownish-yellow; HCl, brownish-yellow precipitate; NaOH, no change; solution in  $H_2SO_4$ , brownish-yellow; on diluting, redder solution and brownish-yellow precipitate.

*Application.*—Diazo-bordeaux yields, when dyed direct on cotton, a reddish-yellow colour of no value, which, however, by diazotising and developing with  $\beta$ -naphthol is converted into a good claret-red shade, very fast to washing, alkalies, and acids, but not to light. By coupling on the fibre with diazotised paranitraniline diazo-bordeaux yields a handsome brown. Silk may be dyed in the same way as cotton.

**DIAZO RUBINE B (Bayer)** yields when diazotised and developed with  $\beta$ -naphthol ruby-red and dark claret shades on cotton, which resemble in fastness those obtained with the preceding dyestuffs.

**BENZO NITROL BORDEAUX G (Bayer).**

Brown powder; aqueous solution, red; HCl, corinth-brown precipitate; NaOH, crimson-red solution; solution in  $H_2SO_4$ , blackish; on diluting, corinth-brown precipitate.

*Application.*—Benzo nitrol bordeaux G is dyed on cotton in the usual way with soda and Glaubersalt, and yields in this way a bluish-claret of little value, which, however, by coupling with diazotised paranitraniline becomes much deeper and also acquires a good fastness to washing, alkalies, and acids, but not to light.

**CONGO-ORANGE R (Berlin, Bayer, Levinstein).**

Tolidine < betanaphthylamine disulphonic acid R.  
phenol (ethylated *after combination*).

Red-orange powder; aqueous solution, red-orange; HCl, brown precipitate; NaOH, soluble orange precipitate; solution in  $H_2SO_4$ , violet-blue; on diluting, brown precipitate.

*Application.*—Congo-orange is dyed on cotton in a boiling bath with the addition of salt only (about 10 per cent. of the weight of the cotton), or with the addition of soap, potash, &c.

It dyes a fine red-orange shade, which is similar to a very red chrome-orange. The fastness to washing is similar to that of the other benzidine colours; the fastness to light is rather better; the colour is not very sensitive to dilute acids. Wool and silk and mixed goods are dyed according to the general methods.

**CONGO-ORANGE G** is a more yellowish brand, of similar properties.

**BENZO-ORANGE R (Bayer, Berlin, Levinstein).**

Benzidine < salicylic acid.  
naphthionic acid.

Brown-red crystalline powder; aqueous solution, red-orange; HCl, red-violet; NaOH, soluble orange precipitate; solution in  $H_2SO_4$ , violet-blue; on diluting, grey-violet precipitate.

*Application and Properties.*—Same as Congo-red. The shade is slightly more reddish and brilliant than that of Congo-orange, and possesses about the same fastness to light, but a greater sensitiveness to dilute acids.

**BENZO FAST ORANGE S** (Bayer).

Regarding the constitution of this dyestuff, see *Benzo fast scarlet*, p. 390.

Reddish-brown powder, not very soluble in water; aqueous solution, orange-red; HCl, red precipitate; NaOH, makes the solution redder; solution in  $H_2SO_4$ , red; on diluting, red precipitate.

*Application.*—Same as Congo-red. Benzo fast orange S is distinguished by its very good fastness to acids, and its exceedingly brilliant shade; its fastness to light and washing is fairly good. Benzo fast orange S yields very good solid shades on unions, and, when dyed on satins in a soap bath, it hardly stains the silk.

**TOLUYLENE ORANGE G** (Oehler-Griesheim).

Tolidine < orthocresol carboxylic acid.  
metatoluylenediamine sulphonic acid.

Brownish-orange powder; aqueous solution, brownish-yellow; HCl, yellowish-brown precipitate; NaOH, soluble orange precipitate; solution in  $H_2SO_4$ , magenta-red; on diluting, brownish precipitate.

*Application.*—Toluylene-orange is dyed in the same way as Congo, and yields chrome-orange shades, from light cream to iron-buff and dark orange. The shades are moderately fast to light, soap, and dilute acids. Toluylene-orange G is a useful padding colour for bottoming in calico-printing. When treated on the cotton fibre with diazotised paranitraniline it yields full red brown shades which are very fast to soap.

**TOLUYLENE ORANGE R** (Oehler-Griesheim).

Tolidine < metatoluylenediamine sulphonic acid.  
metatoluylenediamine sulphonic acid.

Brown-red powder; aqueous solution, orange; HCl, bluish-red precipitate; NaOH, soluble orange precipitate; solution in  $H_2SO_4$ , brown; on diluting, reddish precipitate.

*Application and Properties.*—Same as Toluylene orange G. It dyes a much redder shade of orange, which does not possess the same fastness.

**MIKADO ORANGE G, B, 2 R, 3 R, 4 R** (Leonhardt, Berlin, Bayer).

The Mikado oranges are produced by boiling paranitrotoluene sulphonic acid with alkalis in the presence of oxidisable substances, such as glycerin, tannin, pyrogallie acid, &c. In the same way Mikado yellow and Mikado brown are prepared. The composition of these products has recently been ascertained by A. G. Green (see p. 378).

The general reactions of the Mikado-colours are the following:—Orange to red-brown powders; aqueous solutions, orange; HCl, reddish-brown precipitates; NaOH, soluble orange precipitates; solution in  $H_2SO_4$ , purplish to blue; on diluting, brown precipitates.

*Application.*—Dye cotton in a boiling neutral bath, with the addition of 20 to 30 per cent. of common salt. Alkaline baths are not very well exhausted.

The Mikado oranges yield shades varying from yellow-orange to fiery-red orange, which are very fast to soap, acids, and alkalis, and also to chlorine, and resist light well.

*Unions and Satins.*—The Mikado oranges show very little affinity towards animal fibres; thus, when cotton and wool or cotton and silk are dyed in the same bath by the usual one-bath methods, the shade produced on cotton is much more intense than that produced on wool or silk.

**PYRAMINE ORANGE R, 2 R, and 3 G (B.A.S.F.).***Pyramine Orange R.*—Benzidine sulphonic acid  $\left\{ \begin{array}{l} \text{nitro } m \text{ phenylene diamine.} \\ \text{nitro } m \text{ phenylene diamine.} \end{array} \right.$ *Pyramine Orange 2 R.*—Benzidine  $\left\{ \begin{array}{l} \text{nitro } m \text{ phenylene diamine.} \\ \beta\text{-naphthylamine disulphonic acid R.} \end{array} \right.$ *Pyramine Orange 3 G.*—Benzidine  $\left\{ \begin{array}{l} \text{nitro } m \text{ phenylene diamine} \\ \text{phenylene diamine disulphonic acid.} \end{array} \right.$ 

*Pyramine Orange R.*—Strawberry-coloured, very sparingly soluble powder; aqueous solution, brownish-orange; HCl, brownish-red precipitate; NaOH, redder solution and soluble precipitate; solution in  $\text{H}_2\text{SO}_4$ , brown; on diluting, redder and brown precipitate.

*Pyramine Orange 2 R* is a red-brown powder more soluble than "R," and showing similar reactions, with the exception that it dissolves in concentrated sulphuric acid with a blue colour.

*Pyramine Orange 3 G* is a pale yellowish-brown powder, more freely soluble than "R," and possessing similar, more yellowish reactions.

*Application.*—Cotton is dyed with the addition of salt or Glaubersalt. Pyramine orange R yields a fiery red-orange of very good fastness to light, washing, alkalis, acid, and chlorine. Pyramine orange 2 R is redder in shade, and less fast to acids, but in all other respects equal to the "R" brand. Pyramine orange 3 G dyes a yellowish-orange, equal to "R" in fastness to light, washing, and alkalis, but less fast to acids and chlorine.

Unions are dyed very well with Pyramine orange 2 R, which may also be used on wool, whilst Pyramine orange R and 3 G are dyed with advantage on half-silk in slightly alkaline baths.

**ALKALI ORANGE G (Dahl).**

Reddish powder; aqueous solution, light brown; HCl, brownish precipitate; NaOH, dark brown solution and soluble precipitate; solution in  $\text{H}_2\text{SO}_4$ , brown; on diluting, brown and brown precipitate.

*Application.*—Alkali orange G is dyed on cotton like Congo-red, and yields a moderately fast yellowish-orange. It is dyed on unions in a neutral bath, and on satins with the addition of soap, and yields fairly solid shades.

**DIAMINE ORANGE B (Cassella).**

Brown powder; aqueous solution, brown; HCl, orange-brown precipitate; NaOH, redder solution and soluble brown precipitate; solution in  $\text{H}_2\text{SO}_4$ , orange-red; on diluting, brown precipitate.

*Application.*—Diamine orange B is dyed on cotton with the addition of Glaubersalt and soda, and is chiefly used for mixtures. It yields a full reddish-orange, which is fairly fast to washing, and moderately fast to light; it is not altered by acids, but becomes brownish under the action of alkalis. By treatment with copper sulphate (alone or together with bichromate) the shade becomes browner and faster to light and also to washing. Wool and silk may be dyed by the usual methods with the addition of acetic acid. Unions are dyed in a neutral salt bath, and satins with the addition of soap by the usual methods; the animal fibres being dyed the same shades as the cotton, and nearly to the same depth; hence Diamine orange B is very valuable for dyeing mixed goods.

**DIAMINE ORANGE G and D (Cassella).**

Brownish powder; aqueous solution, brown; HCl, soluble dark brown precipitate; NaOH, redder solution and soluble reddish-orange precipitate; solution in  $\text{H}_2\text{SO}_4$ , violet ("G") or blue ("D"); on diluting, olive-yellow precipitate ("G"), or brown precipitate ("D")



**Application and Properties.**—Cotton is best dyed in a neutral or in a feebly alkaline bath with the addition of 20 to 30 per cent. common salt or Glaubersalt; alkaline baths are less well exhausted than neutral baths. Diamine orange G dyes a yellowish-orange, and "D" a red-orange of very good fastness to light, soap, alkalies, acids, and chlorine.

Unions are dyed in a neutral salt bath, and satins with the addition of soap and phosphate of soda by the usual one-bath methods. In both cases the animal fibre is stained but slightly, whereas a full shade is produced on cotton, and therefore the two dyestuffs are very valuable for dyeing cotton in mixed goods.

#### DIANIL ORANGE G (M.L.B.).

Bright reddish-brown powder; aqueous solution, orange-brown; HCl, soluble orange precipitate; NaOH, deeper and redder solution; solution in H<sub>2</sub>SO<sub>4</sub>, yellowish-brown; on diluting, soluble orange precipitate.

**Application.**—Cotton is dyed in a neutral or feebly alkaline salt bath a bright yellowish-orange, which is fairly fast to light and washing, and good to acids and alkalies. Treatment with copper sulphate improves the fastness to washing. The dyestuff is readily soluble, and useful for self shades and for the production of mode shades, browns, and olives. Unions and satins are dyed by the one-bath methods, the cotton being dyed deeper than the wool or silk.

#### DIANIL ORANGE N (M.L.B.).

Dianile orange N is chiefly dyed on cotton, and yields yellowish-orange or buff shades which are fairly fast to washing, acids, and alkalies, and are converted by coupling with diazotised *p* nitraniline (Azophor red P N) in a full reddish-brown of good fastness to washing.

#### DIRECT ORANGE 2 R (Kalle) or G (Geigy)

*Direct orange 2 R* is obtained by the reduction of *Direct yellow G* (see below), and seems to be *azostilbenedisulphonate of sodium*. It is probably identical with *Direct orange G*, and also identical or very similar to *Mikado orange*, as are also some of the following dyestuffs.

Brown powder; aqueous solution, red-brown; HCl, soluble dark brown precipitate; NaOH, soluble precipitate and redder solution; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, dark brown precipitate.

**Application and Properties.**—Same as *Mikado orange*. The shade is a bright reddish-orange.

#### CHICAGO ORANGE 2 R (Geigy).

Chicago orange 2 R is the product of the condensation of paranitrotoluidine sulphonic acid, and probably an azo-compound of nitrosostilbene disulphonic acid and benzidine.

Brown powder; aqueous solution, brownish-orange; HCl, brown flocculent precipitate; NaOH, no change; solution in H<sub>2</sub>SO<sub>4</sub>, red-violet; on diluting, brown flocculent precipitate.

**Application and Properties.**—Same as *Mikado orange*. The shade is a good orange.

A number of more yellowish brands of Chicago orange are also found in commerce.

#### DIPHENYL ORANGE 2 R and 2 G (Geigy).

These products are produced analogously to the two preceding dyestuffs, in the case of the RR brand paranitrotoluene sulphonic acid being condensed with paraphenylenediamine.

*Diphenyl orange 2 R.*—Light brown powder; aqueous solution, orange-yellow; HCl, bluish-black precipitate; NaOH, soluble orange precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, cherry-red; on diluting, bluish-black precipitate.

**Application and Properties.**—Both products are dyed on cotton with

the addition of Glaubersalt, and on satin with the addition of soap. Diphenyl orange R R dyes a very reddish-orange which is fairly fast to light, soaping, and alkalies, but becomes duller by the action of acids. When diazotised on the fibre, and developed with  $\beta$ -naphthol or toluylene diamine, it yields claret shades or reddish-browns respectively, of fairly good fastness to soaping. The "G G" brand dyes a yellowish-orange, fairly fast to light, washing, and acids, which is reddened by alkalies.

**POLYPHENYL ORANGE R EXTRA** (Geigy) also belongs to the group of the preceding colouring matters, and possesses similar properties. The shade is that of a medium orange.

#### **TITAN ORANGE.**

Brown powder; aqueous solution, light brown; HCl, olive-black precipitate; NaOH, little change; solution in  $H_2SO_4$ , violet-blue; on diluting, an olive-black precipitate and then a brown-yellow solution.

*Application.*—Cotton is dyed in a neutral bath with the addition of 15 to 20 per cent. salt; a medium orange is obtained of fairly good fastness to light and washing, and good fastness to alkalies, acids, and chlorine. When dyed on mixed goods, the animal fibre is hardly stained, especially when the colour is applied in the cold with a bath containing 1 per cent. soda ash and 25 per cent. salt.

#### **CHLOROPHENINE ORANGE G O, R O, and R R** (Clayton).

These dyestuffs are reduction products of Curcuphenine (p. 407).

Red powder; aqueous solution, orange; HCl, dark brown precipitate; NaOH, little change; solution in  $H_2SO_4$ , violet (G O) or blue (R O and R R); on diluting, brown precipitate.

*Application.*—Cotton is best dyed in a boiling bath with the addition of salt. Chlorophenine orange G O dyes a fine yellowish-orange, the brands R O and R R redder oranges of good fastness to light, washing, alkalies, acids, and chlorine. Wool and silk may be dyed in a neutral or feebly acid bath. The dyestuffs are also recommended for the dyeing of unions and satins, the vegetable and the animal fibre being dyed nearly the same shade.

#### **STILBENE ORANGE 4 R** (Clayton).

Red-brown powder; aqueous solution, orange-brown; HCl, olive-black precipitate; NaOH, soluble red-orange precipitate; solution in  $H_2SO_4$ , blue; on diluting, olive-black precipitate.

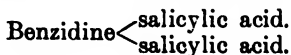
*Application and Properties.*—Similar to the preceding colouring matters. Stilbene orange 4 R dyes a bright reddish-orange.

#### **CHLORAMINE ORANGE G** (Bayer).

Brown powder; aqueous solution, reddish-brown; HCl, soluble black-brown precipitate; NaOH, makes the solution darker and slightly redder; solution in  $H_2SO_4$ , blue; on diluting, soluble black-brown precipitate.

*Application.*—Chloramine orange G resembles the preceding colouring matters. It is dyed on cotton in a neutral salt bath, and yields yellowish-orange shades of very good fastness to light, washing, and chlorine, which are also fairly fast to acids. By coupling with diazotised paranitraniline the shade becomes yellower, and is improved in fastness to washing. When dyed with the addition of soap, it chiefly colours the cotton, leaving the silk nearly unstained.

#### **CHRYSAMINE G** (Bayer, Berlin, Leonhardt, Levinstein).



Brown-yellow powder or yellow paste, sparingly soluble in water; aqueous solution, brownish-yellow; HCl, brown-yellow precipitate; NaOH, soluble

orange-red precipitate; solution in  $H_2SO_4$ , violet-red; on diluting, brown precipitate.

*Application.*—In dyeing with Chrysamine calcareous water must be avoided or purified before the solution of the dyestuff is added. Chrysamine is extremely sensitive towards copper salts, being turned thereby into a brownish-orange; hence it must not be brought into contact with copper, and no copper vessel should be used in dyeing. Chrysamine forms lakes with chromium, and can be dyed on the vegetable and animal fibres with the aid of this mordant. The shades are very fast to light, but not perfectly fast to soap.

Cotton is dyed with the addition of 10 per cent. phosphate of soda and  $2\frac{1}{2}$  per cent. of soap. A reddish shade is obtained which is exceedingly fast to light and resists washing and dilute acids well; alkalies turn the shade into red; but the original colour is restored by washing. Owing to its good fastness to light Chrysamine may be used for padding cream shades on piece goods, and it is also very suitable to serve as a mordant for basic colours. Chrysamine is readily discharged by reducing discharges.

Wool and silk may be dyed with Chrysamine in a neutral, alkaline, or acid bath. The dyestuff, however, is not very valuable for these fibres and also not for unions.

Satin is dyed with the addition of sodium sulphate and soap, fairly solid shades being obtained.

**CHRYSAMINE R** is the tolidine compound, corresponding to the G brand and behaves very similarly. It dyes a more reddish shade of yellow.

**KRESOTINE YELLOW G and R** (Oehler-Griesheim, Bayer) are analogous to Chrysamine G and R, being the corresponding compounds of cresol carboxylic acid and possessing nearly the same properties. They also yield very similar shades of equal fastness.

#### **CARBAZOL YELLOW (B.A.S.F.)**

Diamidocarbazol  $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{salicylic acid.} \end{array} \right.$

Yellow-brown powder; aqueous solution, dark orange; HCl, dark brown precipitate; NaOH, dark-orange colour; solution in  $H_2SO_4$ , blue; on diluting, brownish-black precipitate.

*Application* same as Chrysamine G. Carbazol yellow yields golden-yellow shades, which are fairly fast to light and soap, but sensitive to dilute acids and alkalies. It yields on chromed wool shades which are similar to fustic; they are less fast to light than fustic, but very fast to soap.

#### **COTTON YELLOW G (B.A.S.F.)—BENZO FAST YELLOW 5 G L (Bayer).**

This dyestuff is produced by combining diazotised para-amidoacetanilide with salicylic acid, eliminating the acetyl group and subjecting the product to the action of phosgene gas.

Light-yellow powder; aqueous solution, dirty yellow; HCl, dark brown precipitate; NaOH, soluble orange-yellow precipitate; solution in  $H_2SO_4$ , orange-yellow; on diluting, at first violet, then dark brown precipitate.

*Application and Properties.*—Same as Chrysamine G. The shade is canary-yellow, and is changed by dilute acids. Cotton yellow G serves chiefly for pure yellow shades fast to light. It can also be fixed on chromium mordant, when it will be very fast to soaping.

#### **PYRAMINE YELLOW R (B.A.S.F.)**

Red-brown powder; aqueous solution, yellowish-brown; HCl, brown precipitate; NaOH, no change; solution in  $H_2SO_4$ , yellow; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a neutral or slightly alkaline bath with

the addition of salt, and yields a reddish shade of yellow which is fairly fast to light and washing and resists acids and alkalis well. Wool may be dyed in a neutral or feebly acid bath. The dyestuff is also useful for mixed goods, both fibres being dyed the same shade, when dyed by the ordinary methods (pp. 386 and 387).

**ALKALI YELLOW** (Dahl) or **COTTON YELLOW R** (B.A.S.F.), or **ORIOLE** (Geigy).

Under these different names an azo-dyestuff is sold which is prepared by the action of diazotised Primuline on salicylic acid.

Brownish-yellow powder; aqueous solution, orange-yellow; HCl, yellow precipitate; NaOH, soluble orange precipitate; solution in  $H_2SO_4$ , red-orange; on diluting, yellow precipitate. This dyestuff forms insoluble lakes with chromium oxide, like many other derivatives of salicylic acid; use may be made of this property in calico-printing.

*Application.*—Same as Chrysamine G. The shade is a reddish-yellow. Alkali yellow is fairly fast to soap, but not to light; it is not affected by dilute acids, but is reddened by alkalis.

**ALKALI YELLOW R** (Dahl).

Benzidine  $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{dehydrothiitoluidine sulphonic acid.} \end{array} \right.$

Brown-yellow powder; aqueous solution, yellow; HCl, brownish-yellow precipitate; NaOH, orange-red precipitate; solution in  $H_2SO_4$ , brown-red; on diluting, brownish-yellow precipitate.

*Application and Properties.*—Like Alkali yellow (see above).

**DIANIL YELLOW** (M.L.B.)

Products of combinations of Primuline or dehydrothiitoluidine sulphonic acid with acetacetic ether.

The various brands of Dianil yellow—viz., 3 G, G, R, and 2 R—show nearly the same reactions. Dirty yellow or reddish powder; aqueous solution, yellow-brown or reddish-brown; HCl, yellowish or reddish-brown precipitate; NaOH, makes the solution more reddish; solution in  $H_2SO_4$ , yellowish-brown or reddish-brown; on diluting, brownish precipitate.

*Application.*—The Dianil yellows are dyed on cotton in a neutral bath with the addition of 10 to 25 per cent. salt or Glaubersalt. Dianil yellow 3 G yields a greenish-yellow, the "G" brand a medium yellow, and "R" and "2 R" fine golden-yellow shades. The two latter are very fast to light, fairly fast to washing, and not sensitive to acids and alkalis. The "G" and "3 G" brands are not very fast to light, but equal the redder brands in fastness to washing, acids, and alkalis. Treatment with copper sulphate and bichromate enhances the fastness to light and washing, but dulls the shade.

**TOLUYLENE YELLOW** (Oehler-Griesheim).

Toluylene diamine sulphonic acid  $\left\{ \begin{array}{l} m \text{ nitrophenylene diamine.} \\ m \text{ nitrophenylene diamine.} \end{array} \right.$

Light-yellow powder; aqueous solution, yellowish-brown; HCl, brown precipitate; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , brown; on diluting, lighter and brown precipitate.

*Application and Properties.*—Toluylene yellow is dyed on cotton in a neutral bath with the addition of 20 per cent. salt, and yields a pure reddish-yellow of very good fastness to washing, acids, and chlorine; it is not fast to light, and is slightly reddened by alkalis.

**SALICINE YELLOW G** (Kalle).

Yellow-brown powder; aqueous solution, yellow-brown; HCl, brownish

precipitate; NaOH, makes the solution redder, and produces a soluble precipitate; solution in  $H_2SO_4$ , orange-red; on diluting, brownish precipitate.

*Application and Properties.*—Like Chrysamine G. Salicine yellow G is recommended both as a direct cotton colour and as an acid chrome dyestuff fast to milling on wool.

#### TITAN YELLOW Y and R (Holliday).

Brown powder; aqueous solution, brownish-yellow; HCl, reddish-yellow (Y) or brown (R) precipitate; NaOH, soluble red or orange precipitate; solution in  $H_2SO_4$ , scarlet; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a boiling bath with the addition of salt. Titan yellow Y yields a chrome-yellow shade fairly fast to light and washing and fast to acids, but reddened by alkalies. The R brand dyes an orange-yellow shade of about the same fastness to light and washing, which is reddened by acids and alkalies.

Wool and Silk may be dyed with both brands in an acetic acid bath. Wool may be dyed with Titan yellow Y on a chrome mordant.

#### DIAMINE YELLOW N (Cassella).

Ethoxybenzidine  $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{phenetol.} \end{array} \right.$

This dyestuff is produced by combining diazotised ethoxybenzidine with salicylic acid and phenol, and subsequently ethylating the tetrazo-compound.

Brown yellow powder or yellow paste, not very soluble in water; aqueous solution, yellow; HCl, dark greenish-yellow precipitate; NaOH, reddish-yellow precipitate; solution in  $H_2SO_4$ , violet; on diluting, dark greenish-yellow precipitate.

*Application and Properties.*—Same as Chrysamine G (also as to fastness). The shade is similar to that of Chrysamine R.

#### DIAMINE GOLD (Cassella).

1 : 5 Naphtylene diamine disulphonic acid  $\left\{ \begin{array}{l} \text{phenetol.} \\ \text{phenetol.} \end{array} \right.$

Orange-yellow powder; aqueous solution, orange-yellow; HCl, brown precipitate; NaOH, soluble orange-yellow precipitate; solution in  $H_2SO_4$ , violet; on diluting, flocculent precipitate, which is at first green, and then becomes brown.

*Application.*—Cotton is dyed in a boiling slightly alkaline bath with the addition of 20 to 30 per cent. salt, and then allowed to feed in the cooling liquor. Diamine gold is useful for the production of light golden-yellow shades which are very fast to light, acids, alkalies, and chlorine, and moderately fast to soaping.

#### DIAMINE FAST YELLOW A (Cassella).

Light-brown powder; aqueous solution, brownish-yellow; HCl, soluble brownish precipitate; NaOH, a similar precipitate; solution in  $H_2SO_4$ , purple; on diluting, brownish-yellow solution and precipitate.

*Application.*—Cotton is best dyed in a neutral bath with the addition of about 30 per cent. salt; a bright reddish-yellow shade is obtained of excellent fastness to washing, acids, and chlorine, and also very good fastness to light; alkalies redden the colour very slightly. Silk may be dyed in a feebly acid bath; the colour is very fast to light, washing, and acids, and withstands the water test on this fibre. Unions are dyed with Diamine fast yellow A in a neutral bath and satins in a slightly alkaline bath. In both cases the cotton is dyed in full shades, whereas the wool is but slightly stained, and remains almost colourless. The dyestuff, therefore, is very valuable for dyeing mixed goods, especially for shading the cotton.

**DIAMINE FAST YELLOW A G G** is a new brand of similar character which dyes much more greenish-yellow shades.

**DIAMINE FAST YELLOW B** and **F F** (Cassella).

These yellows are obtained by the action of an alkaline solution of hypochlorite on dehydrothiolumidine sulphonic acid or analogous compounds.

Brownish powder; aqueous solution, brown; HCl, brown precipitate; NaOH, soluble orange precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, dull red; on diluting, yellow solution and brownish-yellow precipitate.

*Application.*—Cotton is dyed in a slightly alkaline or in a neutral bath with the addition of 15 to 30 per cent. salt. Diamine fast yellow F F yields a fairly bright greenish-yellow, the "B" brand a duller yellow. Both dyestuffs level very well and are exceedingly fast to light, acids, alkalis, and chlorine, and also possess very good fastness to washing. Wool and silk may be dyed in neutral or slightly acid baths, the shades on these fibres possessing excellent fastness in almost every respect. Unions are dyed in neutral baths and satins in slightly acid baths, the cotton being dyed slightly fuller than wool or silk, but the same shade; thus Diamine fast yellow is very useful for dyeing mixed goods.

**OXYPHENINE** (Clayton). **CHLOROPHENINE YELLOW Y** (Clayton). **CHLORAMINE YELLOW** (Bayer). **COLUMBIA YELLOW** (Berlin).

These dyestuffs are very similar to each other and to the preceding brands. They are produced by the action of chloride of lime, hypochlorites, or other oxidising agents on dehydrothiolumidine sulphonic acid, or on a mixture of this sulphonic acid and Primuline.

Brown or brownish-yellow powder; aqueous solution, brown or brownish-yellow; HCl, brown or brownish-yellow precipitate; NaOH, soluble brownish precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, dull red; on diluting, brownish-yellow precipitate.

*Application.*—Cotton is dyed with the addition of 10 to 20 per cent. salt, and with or without 2 per cent. soda ash. Wool is dyed in a neutral bath with 10 per cent. sodium sulphate, which may be gradually acidulated with acetic acid. Silk is dyed in an acidulated bath of boiled-off liquor. Unions are best dyed in a neutral bath with the addition of salt, and satins in a soap bath according to the general instructions (p. 386), whereby the vegetable fibre is dyed the same shade, but deeper than wool or silk. Oxyphenine and the other above-named dyestuffs yield on the various fibres reddish-yellow shades, which are not very brilliant nor very full, but possess exceedingly good fastness to light and air, acids, alkalis, chlorine, and stoving. They are also very fast to washing on cotton, and bleed but slightly into white; their fastness to milling on wool is very satisfactory, and on silk they withstand the water test rather well. In general, they belong to the fastest dyestuffs at the disposal of the dyer.

**DIRECT FAST YELLOW B** (Leonhardt) is similar to the preceding dyestuffs in chemical reactions and tinctorial properties.

**BRILLIANT YELLOW** (Leonhardt, Berlin, Bayer). **PAPER YELLOW 3 G** (B.A.S.F.).

Diamidostilbene disulphonic acid  $\left\{ \begin{array}{l} \text{phenol.} \\ \text{phenol.} \end{array} \right.$

Light brown (terra-cotta) powder; aqueous solution, reddish-yellow; HCl, dark blue precipitate; NaOH, red-orange colour; solution in H<sub>2</sub>SO<sub>4</sub>, crimson; on diluting, blue precipitate.

*Application.*—Brilliant yellow is dyed in a neutral bath, or in an acid bath which is prepared with 2½ per cent. of acetic and 10 to 50 per cent. of common salt. Good results are obtained by dyeing at 70° C.



solution or precipitate; NaOH, redder solution and soluble precipitate; solution in  $H_2SO_4$ , orange to red; on diluting, yellow or brownish solution or precipitate.

*Application and Properties.*—These very important dyestuffs are dyed on cotton preferably in a neutral or in a feebly alkaline bath with the addition of salt. The various brands yield greenish-yellow shades on cotton which are very fast to light, washing, acids, and chlorine, and not very sensitive to alkalis. The least greenish brand is Mikado yellow.

For unions and satins these dyestuffs are very useful. They dye principally the cotton, and only slightly stain the wool or silk when dyed in a neutral or alkaline bath by the usual methods. Their fastness on the animal fibres is excellent.

**CURCUMINE S** (Leonhardt, Berlin, Bayer). **DIRECT YELLOW G** (Kalle). **SUN YELLOW** (Geigy). **AFGHAN YELLOW** (Holliday).

*Curcumine S* is produced by boiling a solution of paranitrotoluene sulphonic acid with caustic soda. The above-named dyestuffs are probably identical with or very similar to Curcumine S. They are all nearly related to Mikado yellow, &c.

Curcumine S forms a reddish-brown powder; aqueous solution, brownish-yellow; HCl, brown precipitate; NaOH, soluble orange precipitate; solution in  $H_2SO_4$ , violet; on diluting, orange precipitate.

*Application and Properties.*—Same as Mikado yellow, &c.

Similar reactions and tinctorial properties as the Mikado yellows, Curcumine, &c., are shown by the following dyestuffs:—

**DIRECT YELLOW R** (Bayer),  
**DIRECT YELLOW J and R** (Poirrier),  
**POLYPHENYL YELLOW R and 3 G** (Geigy),  
**CHLORANTINE YELLOW R and JJ** (Ch. Ind. Basle),  
**SUN YELLOW G, CHLORAZOL YELLOW 3 G, A** (Holliday),  
**NAPHTHAMINE YELLOW O** (Kalle),  
**DIANILE DIRECT YELLOW S** (M.L.B.),  
**TRIAZOL YELLOW R** (Oehler),

and the following products.

**CURCUPHENINE** (Clayton).

Product of the condensation of paranitrotoluene sulphonic acid with dehydrothiolumidine sulphonic acid in presence of a very dilute solution of caustic soda.

Bright orange-yellow powder; aqueous solution, brownish-yellow; HCl, dark orange-red precipitate; NaOH, little change; solution in  $H_2SO_4$ , dark red; on diluting, brownish precipitate.

*Application and Properties.*—Like the Mikado yellows. It is recommended by the manufacturers to dye unions in a boiling bath containing 2 grms. acetic acid and 20 to 30 grms. Glaubersalt per litre of liquor.

**DIPHENYL CITRONINE G** (Geigy).

Product of the condensation of dinitrodibenzyl disulphonic acid with aniline in the presence of caustic soda.

Orange powder; aqueous solution, reddish-yellow; HCl, dark brown solution and soluble precipitate; NaOH, soluble yellow precipitate; solution in  $H_2SO_4$ , orange-red; on diluting, yellow solution and dark brown precipitate.

*Application.*—Diphenyl citronine G yields lemon-yellow shades of very good fastness to light, washing, acids, and alkalis. It is very well suitable for dyeing of cotton, unions, and satins, in mixed goods, the cotton being dyed to a deeper shade than wool or silk.



**DIPHENYL FAST YELLOW** (Geigy).

Product of the condensation of dinitrobenzyl-disulphonic acid with Primuline in the presence of caustic soda.

Light brown powder; aqueous solution, orange-brown; HCl, soluble orange-brown precipitate; NaOH, soluble orange-yellow precipitate; solution in  $H_2SO_4$ , red-violet; on diluting, dark brown solution and precipitate.

*Application and Properties.*—Same as Diphenyl citronine G; the shade is a less greenish-yellow.

**DIPHENYL CHRYSOINE G and R R.**

These two dyestuffs also belong to the group of the preceding brands.

Diphenyl chrysoine G, yellowish-brown powder; aqueous solutions, golden-yellow; HCl, black-brown precipitate; NaOH, soluble orange precipitate; solution in  $H_2SO_4$ , violet-red; on diluting, dark brown precipitate. The R R brand shows more reddish reactions, and the solution in sulphuric acid appears blue.

*Application and Properties.*—Same as Diphenyl citronine G; the G brand dyes a lemon-yellow shade, whereas that of the R R brand is reddish-yellow.

**DIPHENYL CHRYSOINE 3 G** (Geigy) is a similar product, and dyes more greenish-yellow shades of equal fastness.

**ARNICA YELLOW** (Geigy).

Azo-compound of nitroso-stilbene disulphonic acid, produced by the condensation of *p*-nitrotoluene sulphonic acid with *p*-amidophenol in the presence of boiling caustic soda.

Brown powder; aqueous solution, brown; HCl, black-brown precipitate; NaOH, no change; solution in  $H_2SO_4$ , red-violet; on diluting, dark brown precipitate.

*Application.*—Same as Diphenyl citronine G. Arnica yellow dyes a fairly reddish-yellow shade which is moderately fast to light and soap, and reddened by alkalis, but good to dilute acids.

**THIAZOL YELLOW** (Bayer). **CLAYTON YELLOW** (Clayton). **MIMOSA** (Geigy). **TITAN YELLOW G** (Holliday). **OXYDIAMINE YELLOW T Z** (Cassella). **NAPHTHAMINE PURE YELLOW G** (Kalle).

Diazoamido-compound produced by the action of the diazotised dehydrothiitoluidine sulphonic acid on dehydrothiitoluidine sulphonic acid. Mimosa, which is probably identical with the other above-named brands, is obtained by the action of ammonia upon diazotised dehydrothiitoluidine sulphonic acid.

Brownish-yellow powder; aqueous solution, dark yellow; HCl, orange precipitate; NaOH, soluble red-orange precipitate; solution in  $H_2SO_4$ , yellow; on diluting, yellow precipitate (on addition of much water only).

*Application.*—Cotton is dyed as with Chrysamine G in a neutral or slightly alkaline bath, and yields a greenish-yellow shade fairly fast to washing, but not to light nor to chlorine, which is slightly reddened by alkalis and acids.

Unions are dyed in a neutral bath, and satins with the addition of soap and soda according to the ordinary methods, the animal fibre being dyed lighter than the cotton.

**NITROPHENINE** (Clayton). **THIAZOL YELLOW R** (Bayer). This dyestuff, which is produced by the action of diazotised *p*-nitraniline on Primuline, is similar to the preceding dyestuff, and yields slightly redder shades of yellow.

**THIAZOL YELLOW 3 G** (Bayer) yields very pure greenish-yellow shades, more greenish than the preceding dyestuffs, which are fairly fast to washing and to acids, fast to alkalis and chlorine, but not fast to light. It is dyed like the preceding dyestuffs. On unions solid shades are obtained. The dyestuff resists reducing discharges well, and is, therefore, useful also in calico-printing.

**THIOFLAVINE S** (Cassella).

Thioflavine S is the sulphonic acid of the basic dyestuff Thioflavine T.

Orange-yellow powder; aqueous solution, golden-yellow; HCl, brownish-yellow precipitate; NaOH, soluble yellow precipitate; solution in  $H_2SO_4$ , light brownish-yellow with a blue fluorescence; on diluting, orange-yellow precipitate; the alcoholic solution is yellow with a green fluorescence.

*Application*.—Cotton, unions, and satins are dyed according to the usual methods in neutral or slightly alkaline baths with the addition of salt or Glaubersalt. Wool and silk are dyed with the addition of 10 per cent. sodium sulphate and eventually some acetic acid to the boiling bath.

Thioflavine S yields a bright lemon-yellow fairly fast to washing and to acids, and not sensitive to alkalies, but rather fugitive to light. It is fast to chlorine, and cannot be discharged nor easily stripped from the fibre. On unions and satins solid shades are obtained; hence Thioflavine S is useful for the production of bright greenish-yellows on these kinds of goods. In calico-printing it is also very serviceable on account of its resistance to discharging agents.

**CHROMINE G** (Kalle).

The composition of this dyestuff, which is produced by melting equal molecules of dehydrothiitoluidine and sulphur, and subsequent methylating and sulphonating, has not yet been established.

Brownish-yellow powder, readily soluble in hot water; aqueous solution, brownish-yellow; HCl, brownish flocculent precipitate; NaOH, soluble yellow precipitate; solution in  $H_2SO_4$ , yellow with a blue fluorescence; on diluting, brownish flocculent precipitate.

*Application*.—Chromine G is dyed on cotton in a mild alkaline bath with the addition of 2 per cent. phosphate of soda and common salt. It yields a fine lemon yellow of fairly good fastness to washing and acids, and not sensitive to alkalies, but rather fugitive to light.

**PRIMULINE. THIOCHROMOGENE.** *Carnotine, Polychromine, Aureoline, Sulphine, Auroline.*

This dyestuff, which is brought into the market under a great variety of names by a number of firms, was discovered by Arthur G. Green,\* at that time chemist to Messrs. Brooke, Simpson & Spiller. Primuline is the sodium sulphonate of the *Primuline-base* which is produced by heating paratoluidine with sulphur to a high temperature. The composition of the Primuline-base is probably  $C_{28}H_{18}N_4S_3$ ,† and the product seems to be formed by the condensation of 4 molecules of paratoluidine and 3 atoms of sulphur; it probably contains

the chromophorous group  $\left\langle \begin{array}{c} N \\ \diagdown \\ C \\ \diagup \\ S \end{array} \right\rangle$ —three times. According to a German

patent of Dahl & Co., which firm discovered the reaction of sulphur on paratoluidine, the Primuline-base is a mixture of bases, and *Thiochromogene* would appear to be a purified and uniform substance in contrast with ordinary Primuline.

Primuline-base is a bright yellow powder which is nearly insoluble in all solvents. The alcoholic solution shows a green-yellow fluorescence. It is an extremely stable compound, not being decomposed when heated to  $400^\circ C$ . Its salts are dissociated by water.

The dyestuff—*i.e.*, the sodium salt of sulphonated Primuline-base—forms a yellow powder, which is very soluble in hot water, but little soluble in alkaline water; aqueous solution, yellow (if very diluted it shows a blue fluorescence); HCl, dark yellow precipitate; NaOH, sparingly soluble light

\* *Journ. Soc. Dyers and Col.*, 1888, p. 39.

† A. G. Green, *Journ. Soc. Dyers and Col.*, 1889, p. 81.

yellow precipitate; solution in  $H_2SO_4$ , pale yellow with a blue fluorescence; on diluting, orange-yellow precipitate.

In contrast to the benzidine colours, Primuline is not decolourised by reducing agents (not being an azo-compound); it cannot be discharged, nor can it be stripped by any practical means. By oxidising agents, such as chromic acid and chloride of lime, it is attacked, but not destroyed. Primuline contains an amido-group; it can therefore be diazotised and combined with naphthol, &c., to form azo-compounds of yellow, red, blue, and other shades. Use is made of this fact to produce the so-called "*ingrain colours*" on the fibre (see below).

*Application.*—Cotton is dyed with Primuline as with the preceding colours in a boiling neutral or alkaline bath; the best addition is common salt or Glaubersalt.

Primuline dyes a greenish-yellow shade, similar to that of the primrose (*Primula*), which is very fast to soap and entirely unaffected by alkalis, but not fast to light. Acetic acid has no action on the shade, mineral acids redden it. Chromic acid changes the shade to olive, whilst an alkaline solution of bleaching-powder or sodium hypochlorite converts it in the cold or on boiling into an orange-yellow, which is very fast to all influences.

Primuline finds its chief application for the production of *ingrain colours* on cotton by means of the diazotising and developing method.

The diazotisation of Primuline and combination with phenols and amines, to produce azo-colours, can be readily performed on the fibre, as discovered by A. G. Green, the inventor of Primuline.\* In this way a variety of shades can be obtained which are characterised by great fastness to soaping, milling, acids, &c., but not to light.

Phenol gives yellow; resorcin, orange; betanaphthol, red, and alphanaphthol, maroon colours; metaphenylene diamine, metatoluylene diamine, and alphanaphthylamine produce browns; and amidoazobenzene a purple shade. The sulphonic acids of betanaphthol, like Schaffer acid or "R salt," may also be used for the production of scarlet to bluish-red colours.

The *ingrain-red* is the most important of the developed shades of Primuline; it possesses great fastness to soaping and milling, acids and alkalis, but is not very fast to light.

On the whole the character of the other *ingrain shades* is the same as that of *ingrain-red* in point of fastness to light, soap, milling, acids, &c.

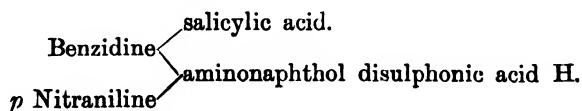
The *ingrain colours* possess also the property of forming lakes with the basic colours and serve as mordants for them.

*Linen.*—The *ingrain colours*, being fast to washing, are of value for the dyeing of linen. The method of procedure is the same as on cotton, less quantity of colour, however, being required to attain the same depth of shade.

*Silk* is also dyed with Primuline by the diazotising method, the developed colours possessing excellent fastness to soap and water.

#### DIAMINE GREEN G, B, CL, DIAMINE DARK GREEN N (Cassella).

Diamine green G is produced by coupling tetrazotised benzidine, with amidonaphthol disulphonic acid H and with salicylic acid, and further coupling with diazotised paranitraniline.



The other above-named dyestuffs possess a similar constitution and show similar reactions.

\* *Journ. Soc. Dyers and Col.*, 1888, p. 40.



Black powder; aqueous solution, dark olive-green; HCl, dark green precipitate; NaOH, brown-black colour; solution in  $H_2SO_4$ , dark violet; on diluting, dark green precipitate.

*Application.*—Benzo olive is dyed on cotton in a boiling neutral bath with the addition of 10 per cent. of salt; if required, alkaline salts may be added to the bath. Benzo olive dyes shades from olive to Russian green, which are fast to soap and acids, and moderately fast to light. The colour becomes brownish by the action of alkalis.

Similar to the preceding green dyestuffs are the following:—

**DIANIL GREEN G** and **DIANIL DARK GREEN B** (M.L.B.).  
**DIPHENYL GREEN G C**, **3 G C**, and **BC** (Geigy).  
**CHLORAMINE GREEN B** (Sandoz).  
**CHLORAZOL GREEN Y** and **B** (Holliday).  
**EBOLI GREEN SJ** and **C W**. **DIRECT GREEN CO** (Leonhardt).  
**NAPHTHAMINE GREEN A** (Kalle).  
**OXAMINE GREEN G** and **B** (B.A.S.F.).  
**DIANOL GREEN A S** and **T** (Levinstein).

#### AZO-BLUE.

Tolidine < alphanaphthol sulphonic acid N W.  
 < alphanaphthol sulphonic acid N W.

Black powder with a metallic lustre; aqueous solution, violet; HCl, violet-blue precipitate; NaOH, soluble dark red precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet-blue precipitate.

*Application.*—Same as Congo-red. Treatment with copper sulphate makes the colour faster to light and more greenish-blue.

Azo-blue dyes a dull reddish shade of blue, which possesses the general character of the salt colours, being fairly fast to washing, but not fast to light. It is not sensitive to dilute acids, but is reddened by alkalis.

**BENZOAZURIN G** (Bayer, Berlin, Leonhardt, Levinstein). **OXAMINE BLUE A** (B.A.S.F.).

Dianisidine < alphanaphthol monosulphonic acid N W.  
 < alphanaphthol monosulphonic acid N W.

Black powder with a bronze lustre; aqueous solution, blue-violet; HCl, blue-violet precipitate; NaOH, crimson colour; solution in  $H_2SO_4$ , blue; on diluting, blue-violet precipitate.

*Application.*—Same as Congo-red. An after-treatment with copper sulphate makes the shade less reddish and essentially faster to light.

Benzoazurin G dyes a reddish indigo-blue shade which is fairly fast to soap, and moderately fast to light; it is not affected by dilute acids, but is reddened by alkalis.

**BENZOAZURIN R** is a mixture of Benzoazurin G and Azo-blue. It dyes a redder shade of blue than Benzoazurin G.

**BENZOAZURIN 3 G** (Bayer, Berlin, Leonhardt, Levinstein).

Dianisidine < alphanaphthol sulphonic acid Cl.  
 < alphanaphthol sulphonic acid Cl.

Greyish-black powder; aqueous solution, blue-violet; HCl, blue-violet precipitate; NaOH, violet-red colour; solution in  $H_2SO_4$ , blue; on diluting, blue-violet precipitate.

*Application and Properties.*—Same as Benzoazurin G. The shade is less reddish, and becomes on treatment with copper sulphate still more greenish.

**BRILLIANT AZURIN 5 G** (Bayer, Berlin, Leonhardt, Levinstein).

Dianisidine  $\left\{ \begin{array}{l} 1 : 8 \text{ dioxynaphthalene 4 sulphonic acid.} \\ 1 : 8 \text{ dioxynaphthalene 4 sulphonic acid.} \end{array} \right.$

Greyish-black powder; aqueous solution, blue-violet; HCl, blue precipitate; NaOH, red colour; solution in  $\text{H}_2\text{SO}_4$ , green-blue; on diluting, dark reddish-blue precipitate.

*Application and Properties.*—Same as Benzoazurin G.

Brilliant azurin 5 G dyes a very pure and brilliant greenish shade of blue, which is fairly fast to soap and moderately fast to light. It is not affected by dilute acids, but is reddened by alkalies. The treatment with copper sulphate increases the fastness to light essentially and makes the shade more greenish.

**BRILLIANT AZURIN B, 2 R, and 5 R** are similar products, which yield less greenish shades of blue; the "5 R" brand dyes a very reddish-blue.

**DIAMINE BLUE 3 R** (Cassella).

Ethoxybenzidine  $\left\{ \begin{array}{l} \text{alphanaphthol sulphonic acid N W.} \\ \text{alphanaphthol sulphonic acid N W.} \end{array} \right.$

Dark powder with a bronze lustre; aqueous solution, violet; HCl, red-violet precipitate; NaOH, crimson colour; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, violet precipitate.

*Application.*—Cotton is dyed in a neutral or weak alkaline bath with the addition of 20 per cent. salt or Glaubersalt. A rather reddish-blue of moderate fastness to light and washing is obtained which is not affected by weak acids, but is reddened by alkalies. The shade becomes violet by a treatment with copper sulphate, and is then very fast to light and rather fast to washing.

Wool and silk are dyed in feebly acid baths according to the directions on p. 385; the shades obtained are very fast to washing and water, and also to alkalies, acids, and stoving, but not very fast to light; by a treatment with copper sulphate they are made very fast to light, but are changed to violet.

Unions and satins are dyed according to the general instructions given on pp. 386 and 387; the shade on wool is slightly redder than that on cotton and the shade on silk still more so.

**DIAMINE BLUE B X** (Cassella). **BENZO BLUE B X** (Bayer). **CONGO BLUE B X** (Berlin).

Tolidine  $\left\{ \begin{array}{l} \text{aminonaphthol disulphonic acid H.} \\ \alpha\text{-naphthol sulphonic acid N W.} \end{array} \right.$

Dark bluish powder; aqueous solution, bluish-violet; HCl, violet precipitate; NaOH, red solution; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, violet precipitate.

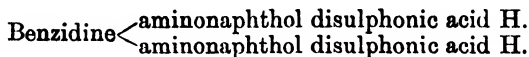
*Application.*—Cotton is dyed in a neutral or weak alkaline bath with the addition of 20 per cent. salt or Glaubersalt. The shade is less reddish than that of Diamine blue 3 R; it is moderately fast to light and fairly fast to washing; weak acids do not affect the shade and alkalies redden it but slightly. Treatments with metallic salts do not improve the colour.

Wool and silk are dyed in feebly acid baths according to the instructions on p. 385; the shades are very fast to washing, water, alkalies, acids, and stoving, and moderately fast to light.

Unions are dyed in a neutral bath as indicated on p. 386; the wool is dyed slightly more reddish than the cotton, but uniform shades are obtained by addition of some Alkali blue.

Satins are dyed with some soap, &c. (p. 387); the dyestuff dyes cotton deeper than silk, and the latter a more reddish shade.

**DIAMINE BLUE 2 B. BENZO BLUE 2 B. CONGO BLUE 2 B X.**



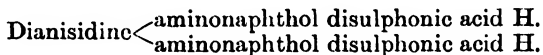
Dark blue powder; aqueous solution, blue-violet; HCl makes the solution redder; NaOH, violet-red solution; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, at first violet and then blue.

*Application and Properties.*—Same as Diamine blue BX. The dyestuff yields a fine blue, more greenish than Diamine blue BX and not sensitive to dilute alkalis. When dyed on satin it dyes both fibres about the same shade, but cotton deeper than silk. On unions uniform shades are produced by the addition of a greenish brand of Alkali blue (3 B to 6 B).

**DIAMINE BLUE 3 B. BENZO BLUE 3 B. CONGO BLUE 3 B.**

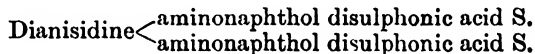
Diamine blue 3 B is the tolidine compound corresponding with the "2 B" brand and possessing nearly the same properties, but dyeing still more greenish shades of blue.

**DIAMINE SKY-BLUE. BENZO SKY-BLUE. CONGO SKY-BLUE.**



This dyestuff is the dianisidine compound corresponding with the two preceding dyestuffs and possessing similar properties. It yields a much purer and also greener shade of blue, which is very valuable for cotton and mixed goods.

**DIAMINE SKY-BLUE FF. BRILLIANT BENZO BLUE 6 B. CHICAGO BLUE 6 B.**



Blue powder; aqueous solution, blue; HCl, soluble blue precipitate; NaOH, violet solution; solution in H<sub>2</sub>SO<sub>4</sub>, greenish-blue; on diluting, blue solution and precipitate.

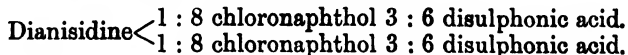
*Application and Properties.*—Same as Diamine sky-blue (see above). The shade is still purer and brighter. By a treatment with copper sulphate a fine greenish-blue is obtained of excellent fastness to light and very good fastness to washing.

**DIAMINE BLUE R W. BENZO BLUE R W. CHICAGO BLUE R W.**

Greyish-blue powder; aqueous solution, blue; HCl, blue precipitate; NaOH, violet solution and precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, greenish-blue; on diluting, violet precipitate.

*Application and Properties.*—Same as Diamine sky-blue FF. The shade is more reddish and also rather bright. It is not much altered by an after-treatment with copper sulphate, except that it also becomes very fast, and thus it is very useful for fast blue and compound shades and especially for shading Diamine sky-blue FF.

**DIAMINE BRILLIANT BLUE G (Cassella).**



Grey-blue powder; aqueous solution, bluish-violet; HCl, soluble violet precipitate; NaOH, cherry-red; solution in H<sub>2</sub>SO<sub>4</sub>, greenish-blue; on diluting, violet.

*Application.*—Diamine brilliant blue G resembles the two preceding blues, and is applied in the same manner. It yields pure reddish-blue and indigo shades which are moderately fast to light, fairly fast to washing, and not sensitive to acids or alkalis. Treatment with copper sulphate makes the colour very fast to light, and enhances the fastness to washing.

**DIAMINERAL BLUE R** (Cassella).

Dark grey powder; aqueous solution, blue; HCl, soluble blue precipitate; NaOH, dark red solution; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Application.*—Diamineral blue R is dyed on cotton by the ordinary methods (p. 381), and yields a good indigo blue of fairly good fastness to light and washing, and good fastness to acids and alkalis. The colour, without being altered much in shade, acquires a very good fastness to light by an after-treatment with copper sulphate, and may also be treated with bichrome to improve the fastness to washing. When unions and satins are dyed by the usual methods (pp. 386 and 387), Diamineral blue R chiefly colours the cotton.

**DIAMINE STEEL BLUE L** (Cassella).

Dark grey powder; aqueous solution, blue; HCl, soluble blue precipitate; NaOH, readily soluble blue precipitate; solution in  $H_2SO_4$ , blue; on diluting, blue solution and precipitate.

*Application.*—Diamine steel blue L is dyed by the ordinary methods, and yields on cotton, greenish-blue shades of fairly good fastness to light and washing, and good fastness to acids and alkalis. When dyed on wool or silk it is also very fast to milling and stoving and to the water test. The dyestuff is also very useful for unions and satins.

**DIAMINE FAST BLUE FFB, FFG, G** (Cassella).

Dark powder; aqueous solution, violet-blue, or in the case of "G," violet; HCl, reddish-blue (FFB) or blue (FFG) or violet (G) precipitate; NaOH, soluble violet, or with FFG greenish-blue precipitate; solution in  $H_2SO_4$ , black-violet, or with FFG, black-green; on diluting, violet, or with FFG, dark green precipitate.

*Application.*—Diamine fast blue is chiefly used on cotton owing to its excellent fastness to light, which is superior to that of vat indigo. It is also fairly fast to washing and fast to acids and alkalis. The colours are dyed by the ordinary methods and level well, especially Diamine fast blue FFB; they may be used for self shades and mixtures for all purposes of cotton dyeing. Unions and satins may also be dyed very fast with Diamine fast blue, the wool being coloured much lighter than the cotton, and the silk being but very slightly stained when dyed by the usual methods (pp. 386 and 387).

**ISAMINE BLUE 6 B, B, and R** (Cassella).

*Isamine Blue 6 B.*—Coppery blue powder; aqueous solution, pure blue; HCl, dark blue precipitate; NaOH, maroon coloured solution and soluble dark precipitate; solution in  $H_2SO_4$ , dull red; on diluting, blue precipitate.

*Application.*—The Isamine blues dye cotton in very bright blue shades, nearly as bright as the Soluble blues. Isamine blue 6 B is the purest brand, and "R" the most reddish one. Cotton is dyed in a neutral bath with 10 to 30 per cent. Glaubersalt and dried. Calcareous water may be acidulated with 1 to 2 per cent. acetic acid. Satins are dyed with combinations of Isamine blue and Diamine blue, Diamine sky-blue FF, or Diamine brilliant blue G, in a dye liquor containing per litre 10 grms. Glaubersalt and 2 grms. soap: rinse, and brighten with acetic acid.

**DIAMINOGENE BLUE G, B B, N A, N B, 3 R N. DIAMINOGENE SKY-BLUE N** (Cassella).

Dark powder; aqueous solution, blue or violet; HCl, dark blue violet



precipitate; NaOH, little change; solution in  $H_2SO_4$ , blue; or with the brands N A, N B, and 3 R N, blackish-green; on diluting, violet precipitate.

*Application.*—The various brands of Diaminogene blue and Diaminogene sky-blue are almost exclusively used on cotton and always fixed by the diazotising and developing process, the direct colour being of no use; whereas those diazotised and developed with beta-naphthol are distinguished by their excellent fastness to light, washing, acids, and alkalis. Diaminogene blue G is used for light greenish-blues, the other brands B B, N A, and N B for indigo blues, 3 R N for very reddish-blues, and Diaminogene sky-blue N as indicated by its name for bright pure blues.

**DIAMINE AZO BLUE R and R R** (Cassella) are of similar character as the Diaminogene blues, and yield when diazotised and developed with beta-naphthol reddish-blues less pure than the former and not quite as fast to light, but also very good to washing. Diamine azo blue R and R R are also very serviceable for direct dyeing.

**CHICAGO BLUE 4 B, B, R, 2 R, 4 R** (Berlin, Bayer).

These dyestuffs are tetrazo-compounds of dianisidine, tolidine, or benzidine, with 1 : 8 amino-naphthol mono and disulphonic acids, and in some cases with another component also.

*Chicago Blue 4 B.*—Blue powder; aqueous solution, blue; HCl, soluble blue precipitate; NaOH, violet solution; solution in  $H_2SO_4$ , green-blue; on diluting, blue solution and precipitate.

*Chicago Blue R.*—Black powder; aqueous solution, blue-violet; HCl, violet precipitate; NaOH, makes the solution redder; solution in  $H_2SO_4$ , blue; on diluting, violet solution and precipitate.

*Chicago Blue 4 R.*—Reddish powder; aqueous solution, reddish-blue; HCl, blue precipitate; NaOH, red-violet solution; solution in  $H_2SO_4$ , blue, on diluting, violet precipitate.

*Application.*—The various brands of Chicago blue are dyed on cotton in a neutral or weakly alkaline bath with the addition of common salt, or Glaubersalt, and yield more or less greenish to reddish-blue shades which are fairly fast to washing, moderately fast to light, and not sensitive to dilute acids and alkalis. The brand "R" possesses the best fastness to washing. "2 R" and "4 R" are inferior in fastness to light and alkalis. The shades of Chicago blue 4 B and B are between those of Chicago blue 6 B and R W (see p. 414), those of the other brands are more reddish. Chicago blue 4 B and B are very fast to light and washing when treated with copper sulphate. Wool and silk are dyed with the various brands in a slightly acid bath, the shades being very fast to washing and water, and also to acids, alkalis, and stoving. The brands 4 B and B are very fast to light, also on these fibres when treated with copper sulphate. Unions and satins may be dyed with the various brands of Chicago blue according to the general methods (pp. 386 and 387); the animal fibre is dyed less deep and slightly redder than the cotton, which difference may be compensated by the addition of Alkali blue. Chicago blue B hardly stains the silk when dyed in an alkaline bath. Chicago blue R is only used for cotton dyeing.

**COLUMBIA BLUE G and R** (Berlin).

These two dyestuffs resemble in their chemical constitution Chicago blue 2 R and 4 R.

*Columbia Blue G.*—Dark blue powder; aqueous solution, dark blue; HCl, soluble blue precipitate; NaOH, violet solution; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Application.*—Columbia blue is used according to the general methods indicated on pp. 381, *et seq.*, for the dyeing of cotton, and also for wool, silk, and mixed tissues. Columbia blue G dyes a medium blue, the "R" a reddish-

blue not very fast to light, fairly fast to washing, and good to acids and alkalis. Silk is but slightly stained when dyed in a soap bath.

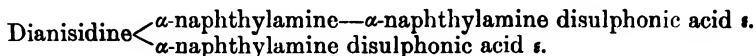
**COLUMBIA FAST BLUE 2 G** (Berlin).

Dark blue powder; aqueous solution, blue; HCl, blue precipitate; NaOH, soluble blue precipitate; solution in  $H_2SO_4$ , bluish-green; on diluting, dark blue precipitate.

*Application and Properties.*—Like Congo fast blue (see below). The shade is a rather greenish-blue.

**CONGO FAST BLUE B and R** (Berlin).

Congo fast blue B.



Dark powder; aqueous solution, blue; HCl, blue precipitate; NaOH, slightly redder solution and soluble precipitate; solution in  $H_2SO_4$ , greenish-blue; on diluting, dark blue precipitate.

*Congo Fast Blue R* is the corresponding tolidine compound and shows similar reactions.

*Application.*—Congo fast blue B and R serve for dyeing cotton, unions, and satins according to the general methods indicated on pp. 381, *et seq.* The brand B dyes a medium blue, "R" a reddish-blue of fairly good fastness to light, washing, and chlorine, and not sensitive to acids or alkalis.

**SOLAMINE BLUE B and R** (Berlin).

*Solamine Blue B.*—Brown powder; aqueous solution, reddish-blue; HCl, blue precipitate; NaOH, makes the solution bluer; solution in  $H_2SO_4$ , dark green-blue; on diluting, blue precipitate.

*Application.*—Solamine blue is dyed on cotton in a feebly alkaline salt bath, and yields navy blue shades which are very fast to light and fairly fast to washing and not sensitive to acids or alkalis.

**ZAMBESI BLUE B X and R X** (Berlin, Levinstein).

Light grey powder; aqueous solution, blue (B) or violet (R); HCl, blue precipitate; NaOH, soluble precipitate and redder solution; solution in  $H_2SO_4$ , bluish-green (B) or blue (R); on diluting, blue precipitate.

*Application.*—Zambesi blue is applied to cotton by the diazotising and developing process only. It is dyed in a feebly alkaline salt bath, and diazotised and developed according to the instructions on p. 382.  $\beta$ -naphthol and naphthylamine ether yield full navy and indigo blues, and toluylene diamine a deep black, which are fairly fast to light and very fast to washing, acids, and alkalis. The fastness to light of the brand B X when developed with  $\beta$ -naphthol or diamine may be enhanced by adding 5 per cent. copper sulphate to the developing bath. Unions and satins may be dyed by the ordinary methods indicated on pp. 386 and 387, the cotton being dyed a deeper shade than the wool.

**ZAMBESI SKY-BLUE 4 B** (Berlin).

Dark powder; aqueous solution, blue; HCl, dark precipitate; NaOH, little change; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Application.*—Zambesi sky-blue 4 B is applied to cotton (like the preceding Zambesi blues) by the diazotising and developing process, and yields with  $\beta$ -naphthol a very fine greenish indigo-blue shade of good fastness to light, washing, acids, and alkalis.

**NAPHTHOGENE BLUE 2 R, 4 R, 6 R** (Berlin).

*Naphthogene Blue 4 R.*—Dark brown powder; aqueous solution, red-violet; HCl, dark blue precipitate; NaOH, soluble dark violet precipitate; solution in  $H_2SO_4$ , blackish-green; on diluting, dark blue precipitate.

*Application.*—The Naphthogene blues are diazotising dyestuffs for cotton, which are dyed in a feebly alkaline salt bath and subsequently diazotised and developed with  $\beta$ -naphthol; they yield very good indigo blue (2 R, 4 R) to dark violet (6 R) shades of very good fastness to light, washing, acids, and alkalies.

**BENZO CYANIN R, B, 3 B (Bayer).**

*Benzo Cyanin B.*—Bluish-grey powder; aqueous solution, blue; HCl, soluble blue precipitate; NaOH, soluble reddish-blue precipitate; solution in  $H_2SO_4$ , greenish-blue; on diluting, reddish-blue solution.

*Application.*—These dyestuffs are chiefly used for cotton, and are dyed best in a neutral bath with the addition of common salt or Glaubersalt. Their shades resemble those of Benzo blue B X, 2 B and 3 B, and possess about the same fastness to washing and acid, but are not fast to light or to alkalies. Benzo cyanin B and 3 B may be after-treated with copper sulphate. Benzo cyanin 3 B is recommended for satins.

**BENZO FAST BLUE B, B N, G, R, 5 R (Bayer).**

*Benzo Fast Blue B.*—Dark grey powder; aqueous solution, violet; HCl, flocculent violet precipitate; NaOH, makes the solution more reddish; solution in  $H_2SO_4$ , dull bluish-green; on diluting, red-violet solution and flocculent precipitate.

*Application.*—The various brands of Benzo fast blue are especially valuable for cotton owing to their very good fastness to light. They are dyed according to the ordinary methods in a weakly alkaline bath, and yield good blue and reddish-blue shades which, in addition to their fastness to light, are fairly fast to washing, and resist acids and alkalies well. The dyestuffs level well and may be used for self-shades and in mixtures. When dyed on unions or satins they chiefly dye the cotton.

**BENZO COPPER BLUE B and 2 B (Bayer).**

*Benzo Copper-blue B.*—Greyish-blue powder; aqueous solution, bluish-violet; HCl, flocculent precipitate; NaOH, red-violet solution; solution in  $H_2SO_4$ , bluish-green; on diluting, bluish-violet solution and flocculent precipitate.

*Application.*—Benzo copper blue is chiefly dyed on cotton in a weakly alkaline salt bath and yields blue shades of moderate fastness. When after-treated with copper sulphate it becomes much faster to light and washing, especially if a mixture of copper sulphate and bichrome is used. The fastness to acids and alkalies is satisfactory. Of the two brands the "B B" is much brighter than the "B" brand.

**BENZO INDIGO BLUE (Bayer, Levinstein).**

Dianisidine  $\left\langle \begin{array}{l} \text{alphanaphthylamine.} \\ 1 : 8 \text{ dioxynaphthalene 4 sulphonic acid.} \end{array} \right.$

Grey powder; aqueous solution, dull blue; HCl, blue precipitate; NaOH, reddish-blue precipitate soluble in water; solution in  $H_2SO_4$ , dark greenish-blue; on diluting, blue precipitate.

*Application.*—Cotton is dyed in a weakly alkaline salt bath. The dye-stuff yields handsome pale and dark indigo shades which are fairly fast to light and soaping and not affected by dilute acids, but reddened by weak alkalies.

**BENZO NAVY BLUE B (Bayer)** is similar to Benzo indigo blue.

**BENZO BLACK-BLUE G, R, 5 G (Bayer, Levinstein).**

*Benzo black-blue G* is produced by combining one molecule of tetrazodiphenyl disulphonic acid with one molecule of alphanaphthylamine, diazotising the product and combining it with two molecules of alphanaphthol sulphonic acid N W.

Black powder; aqueous solution, blue-black; HCl, black-blue precipitate;

NaOH, soluble black-blue precipitate; solution in  $H_2SO_4$ , dark green; on diluting, black-blue precipitate.

*Benzo black-blue R and 5 G* resemble the "G" in composition and reactions.

*Application.*—Benzo black-blue is dyed on cotton in a weakly alkaline bath and yields black-blue shades which are fairly fast to light, washing, acids, and alkalis; the "5 G" brand, however, is somewhat sensitive to alkali. When dyed on satin in an alkaline bath they leave the silk nearly colourless.

**BENZO CHROME BLACK-BLUE B** (Bayer).

Black powder; aqueous solution, dark blue; HCl, soluble blue precipitate; NaOH, makes the solution redder; solution in  $H_2SO_4$ , black-blue; on diluting, redder solution and dark blue precipitate.

*Application.*—Benzo chrome black-blue B is dyed on cotton with the addition of Glaubersalt and some soda and yields a good navy blue, fairly fast to light and washing, and not sensitive to acids or alkalis. By an after-treatment with a mixture of copper sulphate and bichrome, this blue is converted into a blue-black of very good fastness to light, washing, acids, and alkalis. The dyestuff levels well and is very useful for self-shades and for mixtures. It may also be used for unions and satins when it will dye the cotton deeper than wool or silk.

**DIAZURIN B and G** (Bayer).

*Diazurin B.*—Dark blue powder; aqueous solution, brown-red; HCl, violet precipitate; NaOH, soluble red precipitate; solution in  $H_2SO_4$ , blue; on diluting, blue precipitate.

*Application.*—These dyestuffs are used for cotton only, and exclusively by the diazotising and developing process (p. 382). Diazurin B dyes, developed with  $\beta$ -naphthol or ethyl  $\beta$ -naphthylamine, fairly dark indigo shades, the "G" brand black-blue or black-green shades respectively, which are fairly fast to washing and not sensitive to acids or alkalis, but not fast to light.

**DIAZO BLUE, DIAZO RED-BLUE, DIAZO DARK BLUE, DIAZO INDIGO BLUE** (Bayer).

*Diazo Blue.*—Green-black powder; aqueous solution, red-violet; HCl, soluble blue precipitate; NaOH, makes the solution redder; solution in  $H_2SO_4$ , violet; on diluting, blue precipitate.

*Diazo indigo blue B and M.*—Black powder; aqueous solution, dark violet; HCl, soluble blue precipitate; NaOH, little change; solution in  $H_2SO_4$ , blue (B) or blue-violet (M); on diluting, blue (B) or violet (M) precipitate.

*Application.*—These dyestuffs serve, like the preceding, for the dyeing of cotton only by the diazotising and developing process. They are mostly developed with  $\beta$ -naphthol and yield from reddish- to greenish-blues, navy and indigo blues of very good fastness to washing, acids, and alkalis. A number of these shades are also fairly fast to light. Diazo indigo blue M, B R extra, 2 R L, and 4 R L are very fast to light, and Diazo indigo blue 3 R is also very good. Diazo blue 3 R and Diazo indigo blue 4 R L yield very reddish shades of blue, almost violets.

**EBOLI BLUE 6 B, 4 B, 2 B, 2 R, 3 R** (Leonhardt).

The Eboli blues show approximately the following reactions:—Dark powder; aqueous solution, blue to blue-violet; HCl, blue or violet soluble precipitate; NaOH, violet solution; solution in  $H_2SO_4$ , greenish-blue to blue; on diluting, blue or blue-violet precipitate.

*Application.*—The various Eboli blues are chiefly dyed on cotton in a neutral or slightly alkaline bath, with the addition of common salt or Glaubersalt, and yield good blue shades ranging from pure greenish-blue to rather reddish-blue. The shades are fairly fast to washing and alkalis, moderately fast to light, and not sensitive to acids. Unions and satins may be dyed by the general methods (pp. 386 and 387).

**TOLEDO BLUE V (Leonhardt).**

Bluish-grey powder; aqueous solution, dark red-blue; HCl, reddish-blue precipitate; NaOH, makes the solution brighter; solution in  $H_2SO_4$ , dark greenish-blue; on diluting, reddish-blue precipitate.

*Application.*—*Toledo blue V* is dyed on cotton in a neutral or slightly alkaline bath with the addition of common salt or Glaubersalt, and yields a fairly bright reddish-blue, fairly fast to washing, moderately fast to light, and not sensitive to dilute acids or alkalis. By an after-treatment with a boiling solution of chrome alum or bichrome, the colour becomes darker, and faster to washing. Wool is dyed in a neutral or slightly acid bath with the addition of Glaubersalt; the colour may be after-chromed with 2 per cent. bichrome, or the wool may be mordanted with chrome before dyeing. The shade is redder than on cotton, and very fast to milling, alkalis, and acids, and fairly fast to light. Silk is dyed with *Toledo blue V* in acidulated boiled-off liquor, and may be chromed after dyeing; the shade is very fast to washing and water, especially when chromed. Unions and satins are dyed by the ordinary methods (pp. 386 and 387).

**OXAMINE BLUE G, G N, 3 B, B, B G, 3 R, 4 R (B.A.S.F.).**

Oxamine blue 3 R: Tolidine  $\left\langle \begin{array}{l} \beta_1 \text{ amino, } \alpha_3 \text{ naphthol, } \beta_1 \text{ sulphonic acid.} \\ \alpha \text{ naphthol sulphonic acid N W.} \end{array} \right.$

Dark powder; aqueous solution, dark red-violet; HCl, soluble red-violet precipitate; NaOH, redder solution and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet solution and precipitate.

The other brands show similar reactions, the solutions of the G, G N, and 3 B brands in  $H_2SO_4$  are greenish-blue.

*Application.*—Oxamine blue is dyed on cotton by the general methods (p. 381), best in a neutral salt bath, and for light shades with the addition of some soap or soda. Oxamine blue 3 B dyes a very pure shade of blue, the brands G and G N greener shades, and the other brands redder shades of blue. Oxamine blue 3 R dyes a very red blue, and 4 R blue-violet. The shades are fairly fast to washing, moderately fast to light, and not sensitive to dilute acids or alkalis. Oxamine blue B G may be improved in fastness to washing by a treatment with a mixture of copper sulphate and bichrome; the shade becomes a little less bluish by this treatment. Oxamine blue 3 R, 4 R, and B G may be diazotised and developed with beta-naphthol on the fibre, and thereby converted into blue-violet to blue shades of very good fastness to washing. Wool may be dyed especially with Oxamine blue B G, silk with the brand 3 B. Unions and satins can be dyed with Oxamine blue G, G N, 3 B, B, and B G according to the general methods indicated on pp. 386 and 387.

**OXAMINE DARK BLUE B G, R, B R (B.A.S.F.)** are similar to the preceding, and yield darker shades of blue on cotton and unions. The brand R gives a rather reddish blue, B G is brighter, while B R is intermediate in shade.

**OXAMINE COPPER BLUE R R (B.A.S.F.).**

Bluish-grey powder; aqueous solution, reddish-blue; HCl, bluish precipitate; NaOH, reddish-violet solution; solution in  $H_2SO_4$ , bluish-green; on diluting, bluish-violet solution and precipitate.

*Application.*—Oxamine copper blue R R is, as indicated by the name, especially valuable for the treatment with copper sulphate. It is dyed on cotton by the usual method in a neutral or slightly alkaline salt bath, and then treated with copper sulphate. The direct shade is a pure reddish-blue of moderate fastness to light, and fairly fast to washing. The after-treatment with copper sulphate makes the colour very fast to light, and improves the fastness to washing materially. The shades are not sensitive to dilute acids

or alkalis. Satins may also be dyed with Oxamine copper blue; when dyed in a soap bath the silk is but slightly stained.

**PHENAMINE BLUE G, B, R (B.A.S.F.).**

Bluish-black powder; aqueous solution, dark blue (G), blue-violet (B), or red-violet (R); HCl, blue or violet precipitate; NaOH, no change; solution in  $H_2SO_4$ , greenish-black; on diluting, blue or violet precipitate.

*Application.*—The three brands are used for cotton only, and are dyed by the usual methods (p. 381). Phenamine blue G yields greenish-blue, the brand R reddish-blue, while the brand B is intermediate, but darker in shade. The colours are fairly fast to washing, moderately fast to light, and not sensitive to dilute acids or alkalis.

**DIANIL BLUE G, B, R, 2 R, 4 R (M.L.B.).**

*Dianil Blue B.*

Tolidine  $\left\{ \begin{array}{l} 1 : 8 \text{ dioxynaphthalene } 3 : 6 \text{ disulphonic acid.} \\ 1 : 8 \text{ dioxynaphthalene } 3 : 6 \text{ disulphonic acid.} \end{array} \right.$

Greyish-blue powder; aqueous solution, blue; HCl, little change; NaOH, makes the solution redder; solution in  $H_2SO_4$ , greenish-blue; on diluting, red-blue solution.

*Dianil Blue R, 2 R, and 4 R* give similar, but redder, the brand "G" greener, reactions.

*Application.*—The Dianil blues are dyed on cotton in a neutral salt bath, and yield greenish- to reddish-blues, the brand 4 R a not very bright violet. They are fairly fast to washing and alkali, moderately fast to light, and not sensitive to dilute acid. The fastness to washing is materially improved by a treatment with chromium salts. A light treatment in a boiling bath of copper sulphate enhances the fastness to light of the brands G, B, and R, but a severe treatment makes the shades much duller. Unions and satins are dyed by the general methods (pp. 386 and 387).

**DIANIL DARK BLUE R (M.L.B.)** yields navy blue and dark blue shades, which exceed those of the preceding Dianil blues in fastness to light and washing. It may be after-treated with copper sulphate, or diazotised and developed with beta-naphthol, or coupled with diazotised paranitraniline or treated with Solidogene, in order to improve the fastness of the colour.

**TRIAZOL BLUE R, B, 2 B, 3 B (Oehler-Griesheim).**

*Triazol Blue B.*—Grey powder, not very freely soluble in water; aqueous solution, blue-violet; HCl, violet precipitate; NaOH, soluble violet precipitate; solution in  $H_2SO_4$ , greenish-blue; on diluting, blue precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath pure shades of blue, which are very satisfactory to washing, and good to acids and alkalis, but not very fast to light. Unions and satins may be dyed by the one-bath methods.

**TRIAZOL DEEP BLUE B and TRIAZOL INDIGO BLUE (Oehler-Griesheim).**

These two dyestuffs closely resemble the preceding Triazol blues in application and properties, and dye dark blue and indigo blue shades.

**NAPHTHAMINE BLUE 3 R, B, 3 B, 5 B, G E (Kalle).**

*Naphthamine Blue B.*—Greyish-blue powder; aqueous solution, dark violet HCl, soluble violet precipitate; NaOH, red-violet solution; solution in  $H_2SO_4$ , blue; on diluting, violet.

*Naphthamine Blue 5 B.*—Bluish-grey powder; aqueous solution, blue; HCl, soluble blue precipitate; NaOH, redder solution; solution in  $H_2SO_4$ , bluish-green; on diluting, blue.

*Application.*—Naphthamine blue is dyed on cotton in a slightly alkaline bath, with the addition of salt, and yields reddish-blue and blue shades which

are moderately fast to light and fairly fast to washing, and not sensitive to dilute alkalis or acids. Wool and silk may be dyed in feebly acid baths, unions and satins by the ordinary methods (see pp. 385 to 387).

**NAPHTHAMINE DEEP BLUE (Kalle).**

Black-blue powder; aqueous solution, dark violet; HCl, soluble violet precipitate; NaOH, redder solution; solution in  $H_2SO_4$ , blue; on diluting, violet.

*Application and Properties.*—Same as Naphthamine blue. The shade is deeper and not very bright.

**NAPHTHAMINE INDIGO R E (Kalle).**

Greyish-black powder; aqueous solution, dark red-violet; HCl, blue-violet precipitate; NaOH, soluble red-violet precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet.

*Application.*—Naphthamine indigo R E yields, when dyed on cotton with the addition of salt, a dull violet which is converted by diazotising and developing with beta-naphthol into an indigo-blue shade of very good fastness to washing, acids, and alkalis, and moderate fastness to light. When developed with naphthylamine ether a similar, but duller, blue is obtained. By coupling the direct colour with diazotised paranitraniline it yields a handsome violet-brown shade.

**DIPHENYL BLUE 3 G, 2 B, B, 2 R (Geigy).**

*Diphenyl Blue 3 G.*—Grey powder; aqueous solution, blue; HCl, violet precipitate, soluble with a blue colour; NaOH, easily soluble blue precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet solution and precipitate.

*Application.*—Diphenyl blue is dyed on cotton, unions, and satins by the usual methods. The "3 G" brand yields a fairly bright greenish-blue, moderately fast to light and fairly fast to washing, and not sensitive to acids or alkalis. The other brands dye redder shades.

**DIPHENYL INDIGO BLUE (Geigy).**

Blue-black powder; aqueous solution, reddish-blue; HCl, dark blue precipitate; NaOH, redder solution; solution in  $H_2SO_4$ , red-violet; on diluting, blue precipitate.

*Application.*—Diphenyl indigo blue dyes on cotton very good indigo shades of fairly good fastness to light and washing, which are not affected by dilute acids or alkalis. The fastness to washing is greatly enhanced by an after-treatment with bichromate (p. 384).

**ACETYLENE BLUE 3 R, B X, 3 B, 6 B. ACETYLENE SKY-BLUE (Ch. Ind. Basle).**

*Acetylene Blue 3 R.*—Dark brown powder; aqueous solution, dark red-violet; HCl, soluble red-violet precipitate; NaOH, magenta-red solution; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Acetylene Blue 6 B.*—Grey powder; aqueous solution, dark blue; HCl, no change; NaOH, red-violet solution; solution in  $H_2SO_4$ , blue-green; on diluting, blue solution.

*Application.*—Acetylene blue is dyed on cotton with the addition of common salt. The "3 R" brand dyes a violet, the other brands dye fairly pure reddish- to greenish-blue shades, and Acetylene sky-blue a very pure blue, moderately fast to light and fairly fast to washing. The brands 6 B and 3 R, and Acetylene sky-blue, are not affected by dilute acids; the two other brands are slightly reddened. Acetylene blue B X becomes blackish by the action of alkalis; the other brands are slightly reddened.

**DIRECT INDIGO BLUE A (Ch. Ind. Basle).**

Grey powder; aqueous solution, blue; HCl, soluble blue precipitate; NaOH, soluble blue precipitate; solution in  $H_2SO_4$ , blue; on diluting, blue solution and precipitate.

*Application.*—Direct indigo blue is dyed on cotton with the addition of salt, and yields greenish indigo shades which are not very fast to light, but fairly fast to washing, and not sensitive to dilute alkalies or acids. It may also be used for dyeing unions solid shades. On satins, chiefly the cotton is covered.

**DIRECT INDIGO BLUE B N, B N K, and B K** are similar dyestuffs.

**INDIGENE BLUE B B, B, and R** (Ch. Ind. Basle).

Greyish-black powder; aqueous solution, dark red-violet; HCl, soluble violet precipitate; NaOH, redder solution; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, violet solution and precipitate.

*Application.*—Indigene blue is dyed on cotton by the diazotising and developing method. When dyed with salt and a little soda and then diazotised and developed with beta-naphthol on the fibre, it yields reddish-to greenish-blue shades of very good fastness to washing, which are fairly fast to light and not sensitive to dilute acids or alkalies.

**INDAZURIN** (Basle Chemical Co.).—A great number of brands (T S, B, M N, G M, 5 G M, M G R, R M, B X, B B) are found in commerce.

*Indazurin T S, B, and M N, e.g.,* show the following reactions:—Dark powders; aqueous solution, red-violet (T S), blue (B), or blue-violet (M N); HCl, precipitates of the same colour; NaOH, red-violet solutions; solutions in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, red-violet (T S and M N) or blue (B) precipitates.

*Application.*—The Indazurins yield, when dyed on cotton with the addition of salt, greenish to reddish indigo shades which are fairly fast to washing, moderately fast to light, and not sensitive to dilute acids. Some of them are rather sensitive to alkalies; the best in this respect are Indazurin B and 5 G M. The brand T S yields, when diazotised and developed with phenylene diamine, a good black-blue which is slightly reddened by alkalies. Indazurin M N is recommended for satins.

**TRISULPHONE BLUE B and R** (Sandoz).

*Trisulphone Blue B.*—Dianisidine <  $\alpha$ -naphthol (1) trisulphonic (3, 6, 8) acid.  
 $\beta$ -naphthol.

*Trisulphone Blue R* is the corresponding tolidine compound.

Bluish-grey (B) or dark bronzy (R) powder; aqueous solution, blue or blue-violet; HCl, soluble blue precipitate; NaOH, red-violet solution; solution in H<sub>2</sub>SO<sub>4</sub>, greenish-blue; on diluting, blue-violet precipitate.

*Application.*—Trisulphone blue is dyed on cotton in a neutral or slightly alkaline salt bath. When dyed with the addition of alum, the liquor is better exhausted. The "R" brand dyes a reddish-blue, and "B" a more greenish-blue, moderately fast to washing and not sensitive to dilute acids or alkalies. The colours become faster to washing by an after-treatment with a boiling solution of bichrome. Wool and silk may be dyed in a neutral bath or with the addition of acetic acid, the resulting shade being more reddish than that on cotton.

**MELOGENE BLUE B H** (Sandoz).

Benzidine < amino-naphthol sulphonic acid H.  
 xyldine—amino-naphthol sulphonic acid H.

Blue-black powder; aqueous solution, blue-violet; HCl, soluble violet precipitate; NaOH, violet solution; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, violet precipitate.

*Application.*—Melogene blue B H is dyed on cotton with the addition of salt and a little soda, and then diazotised and developed with  $\beta$ -naphthol; it thus yields a good black which is very fast to washing, moderately fast to light, and resists well the action of dilute acids and alkalies. When developed with



resorcinol it yields dark green shades, and with phenylene diamine brownish-blacks.

**CHLORAZOL BLUE 3 R, R, B, 2 B, 3 B, 4 B, 3 G, 6 G, 12 G (Holliday).**

This group of dyestuffs is produced by the action of various diazo-compounds on chloronaphthol sulphonic acid, and shows the following general reactions.

Violet to blue powder; aqueous solution, violet to blue; HCl, makes the solution less reddish or greener; NaOH, makes the solution redder; solution in  $H_2SO_4$ , blue to greenish-blue; and on diluting, less greenish or redder solution.

*Application and Properties.*—The Chlorazol blues are dyed by the usual methods on cotton, and dye red-violet ("3 R") to greenish-blue ("6 G") shades which are moderately fast to washing and light, and are rendered much faster by an after-treatment with copper sulphate. Chlorazol blue 12 G resembles the Titan comos (see below). Wool may be dyed in a neutral or slightly acid bath, the shades obtained possess a fair fastness to milling, and are fast to stoving. Silk is dyed in an acid bath; the shades possess a good fastness to water.

**TITAN BLUE R, 3 B. TITAN NAVY B, 3 B (Holliday).**

These brands resemble the Chlorazol blues in application and properties, but yield darker and less brilliant shades.

**TITAN INGRAIN BLUE (Holliday).**

Blue powder; aqueous solution, bright blue; HCl, violet precipitate; NaOH, makes the solution violet; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Application.*—Titan ingrain blue is dyed on cotton by the usual methods, and diazotised and developed with beta-naphthol.

**TITAN COMO B, 2 B, G, R, and S (Holliday).**

These dyestuffs are naphthylated rosanilines produced according to E.P. 9689, 1893.

Indigo blue powder; aqueous solution, blue; HCl, blue precipitate; NaOH, soluble crimson-red precipitate; solution in  $H_2SO_4$ , brownish-red; on diluting, blue precipitate in blue solution.

*Application.*—Titan como yields exceedingly pure blue shades on cotton, which, however, are not very fast to light or washing. It is best dyed in a bath acidulated with acetic acid. The brand "G" yields the most greenish and "R" the most reddish shades of blue. Silk may be dyed from an acetic acid bath fast to water.

**PARAMINE BLUE B. PARAMINE INDIGO BLUE (Claus & Co.).**

Indigo blue powder; aqueous solution, blue; HCl, violet-blue precipitate; NaOH, red-violet solution and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet-blue precipitate.

*Application.*—The two blues are dyed on cotton in a feebly alkaline salt bath, and yield a fairly bright blue and indigo blue of moderate fastness to light, fairly good fastness to washing, and good fastness to acids; alkalis redden the shades.

**PARAMINE NAVY BLUE R, 2 R. PARAMINE BLUE-BLACK S (Claus & Co.).**

These dyestuffs behave similarly to the preceding Paramine blue, and yield dark navy blue shades; in fastness to light they are inferior to Paramine blue.

**DIANOL BLUE BH (Levinstein).**

Bluish-grey powder; aqueous solution, reddish-blue; HCl, violet precipitate; NaOH, soluble red-violet precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath in very good indigo blue shades of fairly good fastness to light and washing, and good

fastness to acids and alkalis. By diazotising and developing, darker colours are obtained, with beta-naphthol indigo blues and navy blues, and with resorcin or toluylene diamine blacks, which are very fast to washing, acids, and alkalis, and fairly fast to light. Unions and satins are dyed by the general methods indicated on pp. 386 and 387, the vegetable fibre being dyed much deeper than wool or silk.

**DIANOL BLUE G** and **DIANOL SKY-BLUE** (Levinstein) show similar reactions, and are applied in the same way, but for direct dyeings only. Dianol blue G dyes a brighter blue than Dianol blue BH, and Dianol sky-blue a very pure blue, which are moderately fast to light and fairly fast to washing.

**AZO-VIOLET** (Bayer, Berlin, Leonhardt, Levinstein).

Dianisidine < naphthionic acid.  
alphanaphthol monosulphonic acid N W.

Black-blue powder; aqueous solution, red-violet; HCl, blue precipitate; NaOH, crimson colour; solution in  $H_2SO_4$ , blue; on diluting, blue precipitate.

*Application.*—Same as Congo red.

Azo-violet yields a dull blue-violet shade, which is fairly fast to soap, dilute acids, and moderately fast to light and alkalis. By treatment with a boiling solution of copper sulphate, the shade becomes faster to soap and light and less reddish.

**DIAMINE VIOLET N** (Cassella).

Benzidine < gamma-aminonaphthol sulphonic acid.  
gamma-aminonaphthol sulphonic acid  
(combined in acid solution).

Black-brown powder; aqueous solution, red-violet; HCl, violet-black; NaOH, no change; solution in  $H_2SO_4$ , green-blue; on diluting, red-violet precipitate.

*Application.*—Cotton is dyed with the addition of common salt or Glauber-salt in a weakly alkaline or neutral bath. Diamine violet yields a handsome violet shade of rather good fastness to light and washing, and good fastness to acids and alkalis. Wool and silk are dyed in neutral or slightly acid baths, the shades being very fast to light, milling, washing, water, acids, and alkalis. Unions and satins are dyed by the general methods, the cotton being dyed deeper and slightly more bluish than the wool or silk which may be shaded by the various acid or basic violet dyestuffs.

**OXYDIAMINE VIOLET B** (Cassella).

This dyestuff shows similar reactions and tinctorial properties as Diamine violet N, and is used in the same manner. It dyes a more bluish and less bright violet which is also slightly inferior in fastness to light, it has greater covering power, and is chiefly used for deep violets and for clarets.

**DIAMINE HELIOTROPE G, B, O** (Cassella).

*Diamine Heliotrope G.*—Brown powder; aqueous solution, red-violet; HCl, dark precipitate; NaOH, soluble dark precipitate; solution in  $H_2SO_4$ , peacock blue; on diluting, dark precipitate.

*Application.*—Diamine heliotrope is dyed on cotton in a feebly alkaline salt bath, and yields heliotrope and violet shades which are moderately fast to light, fairly fast to washing, and not sensitive to acids or alkalis. Diamine heliotrope G is the reddest brand and "B" dyes the most bluish shades of the three, whilst "O" is intermediate. By diazotising and developing with beta-naphthol good violet-blue shades are obtained, which possess good fastness to washing and resist the light fairly well; they are not sensitive to acids or alkalis, and may also be used for warps to be cross-dyed, especially for warps in pile goods. Unions and satins may be dyed with the Diamine heliotropes by the usual methods.

**HESSIAN VIOLET** (Leonhardt, Berlin, Bayer).

Diamidostilbene disulphonic acid < alphanaphthylamine.  
betanaphthol.

Brown-black powder; aqueous solution, red-violet; HCl, blue precipitate; NaOH, soluble crimson precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, violet precipitate.

*Application.*—Cotton is dyed in a boiling bath, with the addition of 5 per cent. of borax and a small quantity of common salt; it is then passed through soda solution and dried.

Hessian violet dyes a dull red-violet shade, which is rather sensitive to acids and not fast to light; it possesses the fastness to washing and alkalies common to these dyestuffs.

**BENZO VIOLET R** (Bayer, Berlin).

Blackish powder; aqueous solution, red-violet; HCl, soluble violet precipitate; NaOH, red solution; solution in H<sub>2</sub>SO<sub>4</sub>, violet; on diluting, violet precipitate.

*Application.*—Benzo violet R is best dyed on cotton in a neutral salt bath, and yields a nice violet shade of fairly good fastness to washing and acids; it is not very fast to light and is reddened by alkalies. When dyed on satin it chiefly colours the cotton and stains the silk a pale reddish shade.

**BENZO FAST VIOLET R** (Bayer).

Grey powder; aqueous solution, claret-red; HCl, violet solution and flocculent precipitate; NaOH, soluble precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, greenish-blue; on diluting, red-violet solution and precipitate.

*Application.*—Cotton is dyed, in a neutral or feebly alkaline salt bath, a red-violet shade, fairly fast to light and washing, and fast to acids and alkalies. Unions and satins are dyed by the usual methods, the cotton being dyed deeper than the animal fibres.

**CHLORAMINE VIOLET R** (Bayer).

Violet-brown powder; aqueous solution, magenta-red; HCl, flocculent precipitate; NaOH, more yellowish solution; solution in H<sub>2</sub>SO<sub>4</sub>, violet; on diluting, magenta-red.

*Application.*—Cotton is dyed in a neutral salt bath a red-violet shade, which is fairly fast to washing and chlorine, but not very fast to light; the fastness to alkalies and acids is good. The dyestuff may also be used with advantage for satins, the cotton being dyed a deeper shade than the silk.

**TRONA VIOLET B** (Bayer).

Brownish-black powder; aqueous solution, magenta-red; HCl, little change; NaOH, makes the solution more yellowish; solution in H<sub>2</sub>SO<sub>4</sub>, deep bluish-red; on diluting, magenta-red.

*Application and Properties.*—Same as Trona red 3 B (p. 396). Trona violet B dyes on cotton a reddish-violet shade, fast to mineral acids.

**HELIOTROPE B and B B** (Bayer, Berlin, Leonhardt, Levinstein).

*Heliotrope B.*—Dianisidine < methyl naphthylamine deltasulphonic acid.  
methyl naphthylamine deltasulphonic acid.

Dark brown powder; aqueous solution, magenta-red; HCl, violet precipitate; NaOH, soluble crimson precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, violet precipitate.

*Heliotrope B B.*—Benzidine < naphtholsulphonic acid B.  
naphtholdisulphonic acid Sch.

Dark grey powder; aqueous solution, red-violet; HCl, bluish-violet pre-

precipitate; NaOH, redder solution; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

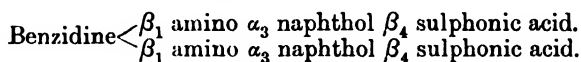
*Application.*—Cotton is dyed, in a feebly alkaline bath, fine heliotrope shades, moderately fast to washing and not sensitive to alkalis; the colours are not very fast to light and become bluer by the action of dilute acids. The shade of Heliotrope B B is more bluish than that of "B."

#### DIAZO VIOLET R (Bayer).

Black-brown powder; aqueous solution, dark red; HCl, dark precipitate; NaOH, yellower solution and soluble precipitate; solution in  $H_2SO_4$ , red-violet; on diluting, dark precipitate.

*Application.*—Diazo violet R is used on cotton exclusively by the diazotising and developing process, and yields, when developed with  $\beta$ -naphthol, a reddish violet which is not quite fast to washing and not very fast to light; it is not sensitive to dilute acids, but reddened by alkalis.

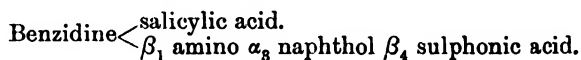
#### OXAMINE VIOLET (B.A.S.F.).



Greyish-black powder; aqueous solution, red-violet; HCl, violet precipitate; NaOH, redder solution and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet solution and violet precipitate.

*Application.*—Oxamine violet yields, when dyed direct on cotton, a violet fairly fast to washing, moderately fast to light, and not sensitive to acids or alkalis. The colour becomes very fast to washing by diazotising and developing; beta-naphthol yields a dark indigo blue, alpha-naphthol a redder blue, ethyl beta-naphthylamine a greener blue, and *m* phenylene diamine a brown; the blue produced with beta-naphthol is of special value.

#### OXAMINE MAROON (B.A.S.F.).



Dark powder; aqueous solution, dark red; HCl, maroon precipitate; NaOH, yellower solution and soluble orange-red precipitate; solution in  $H_2SO_4$ , blue violet; on diluting, maroon precipitate.

*Application.*—Oxamine maroon yields on cotton, in a feebly alkaline bath, violet-brown or maroon shades of little fastness to light and moderately good fastness to washing; it is not sensitive to alkalis, but reddened by acids.

#### AZO-CORINTH (Oehler-Griesheim).

Red-brown powder; aqueous solution, brown; HCl, maroon precipitate; NaOH, cherry-red solution; solution in  $H_2SO_4$ , blue-violet; on diluting, maroon precipitate.

*Application.*—Azo-corinth is dyed on cotton in a feebly alkaline bath, and yields maroon shades of fairly good fastness to washing; it is not very fast to light, acids, or alkalis.

#### TRIAZOL VIOLET B (Oehler-Griesheim).

Violet-grey powder, sparingly soluble in water; aqueous solution, violet; HCl, violet precipitate; NaOH, little change; solution in  $H_2SO_4$ , peacock blue; on diluting, violet precipitate.

*Application.*—Triazol violet B is dyed on cotton in a feebly alkaline salt bath, and yields bluish-violet shades, which are fairly fast to washing, but not very fast to light; it is not sensitive to acids, but becomes redder by the action of alkalis.

**TRIAZOL VIOLET R** (Oehler-Griesheim) is more soluble than the "B" brand, and dyes more reddish shades. It is useful for cotton and also for satins, leaving the silk nearly colourless.

**DIPHENYL VIOLET R** (Geigy).

Dark red-brown powder; aqueous solution, magenta-red; HCl, violet precipitate, soluble with a red colour; NaOH, more yellowish solution and soluble precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, violet; on diluting, violet precipitate.

*Application.*—Diphenyl violet R dyes on cotton a reddish-violet shade, moderately fast to light, fairly fast to washing, and not sensitive to acids or alkalis.

**CHLORANTINE LILAC B** (Ch. Ind. Basle).

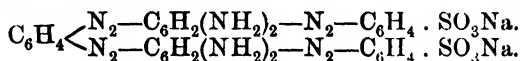
Dark violet powder; aqueous solution, red-violet; HCl, red-violet precipitate; NaOH, redder solution and soluble gelatinous red-violet precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, violet; on diluting, claret-red solution and violet red precipitate.

*Application.*—Chlorantine lilac yields on cotton, unions, and satins, when dyed by the usual methods, very fine lilac shades of fairly good fastness to light and washing, and good fastness to alkalis, acids, and chlorine.

**TRISULPHON VIOLET B** (Sandoz).

Dark bronzy powder; aqueous solution, violet; HCl, soluble blue-violet precipitate; NaOH, violet-red solution; solution in H<sub>2</sub>SO<sub>4</sub>, greenish-blue; on diluting, violet precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath a pure bluish-violet, not very fast to light, and moderately fast to washing; acids redden the shade, whilst alkalis make it slightly more bluish. Boiling with bichromate darkens the shade, and makes it faster to washing. Wool and silk are dyed in neutral baths, or with the addition of acetic acid, the shades being redder on these fibres than on cotton.

**BENZO BROWN G** (Bayer, Levinstein).

Benzo brown G is produced by combining diazotised sulphanilic acid with Bismarck brown. Dark brown powder; aqueous solution, orange-brown; HCl, brown precipitate; NaOH, soluble brown precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, black-brown; on diluting, at first violet solution, then brown precipitate.

*Application.*—Benzo brown is dyed at the boiling temperature either in a neutral bath, with the addition of about 10 per cent. of common salt, or in an alkaline bath, with the addition of 5 per cent. of soda and 2 per cent. of soap. It yields a yellowish shade of brown, fairly fast to soap and to dilute acids and alkalis, but not to light. By coupling with diazotised paranitraniline a good reddish-brown shade is obtained, which is much more intense and faster to washing than the direct dye.

**BENZO BROWN B** (Bayer, Levinstein).

This dyestuff is produced analogously to the preceding by using naphthionic acid instead of sulphanilic acid. It shows the same reactions and properties, and is dyed in the same way. The shade is slightly less yellowish.

**BENZO BROWN BR, BX, NB, NBX, NBR, R EXTRA, RC, D 3 G, G G, BENZO DARK BROWN EXTRA** (Bayer) are similar dyestuffs, which yield various shades of bluish, reddish, or yellowish-browns. Some of these brands—*e.g.*, Benzo brown R extra—may also be fixed on the fibre by coupling.

**DIRECT FAST BROWN G G and B. DIRECT BRONZE BROWN** (Bayer).

Direct fast brown B is a black-brown powder; the two other brands are yellowish-brown powders. All three brands yield dark brown solutions; HCl, brown precipitate; NaOH, makes the solution redder, and produces a soluble precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, blue-violet; on diluting, violet-brown precipitate.

*Application.*—The three brands are dyed on cotton to best advantage in a neutral salt bath, and yield browns which are fairly fast to washing, acids, and alkalis, and moderately fast to light. The shade of Direct fast brown G G is chestnut-brown, that of "B" is a deep violet-brown, whilst Direct bronze brown dyes more olive or bronze brown shades. Direct fast brown B may be fixed by coupling with diazotised *p* nitraniline.

**TOLUYLENE BROWN** (Griesheim-Oehler. Bayer).

Several brands of Toluylene brown (G, R, M, and B) are in the market. For the production of the "G" brand toluylene diamine sulphonic acid is diazotised and combined with metaphenylene diamine. This compound is converted into other brands by combination with diazotised sulphanilic acid or orthotoluidine sulphonic acid or naphthylamine sulphonic acid.\*

*Toluylene Brown G.*—Brown powder; aqueous solution, brown; HCl, yellowish-brown precipitate; NaOH, soluble yellowish-brown precipitate; solution in  $H_2SO_4$ , red-brown; on diluting, yellowish-brown precipitate.

*Toluylene Brown R.*—Dark brown powder; aqueous solution, brown; HCl, red-brown precipitate; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , brown-violet; on diluting, red-brown precipitate.

*Application.*—Cotton is best dyed in a neutral salt bath. Toluylene brown G dyes a yellowish-brown, "R" a fine chestnut-brown, M and B bluer shades of brown which are fairly fast to soap, acids, and alkalis, but not very fast to light. Unions and satins are dyed by the usual methods.

**NEW TOLUYLENE BROWN B, B B O, and M, &c.**, are similar to the preceding browns.

**PLUTO BROWN R** (Bayer).

Brown powder; aqueous solution, dark red-brown; HCl, dark brown-red solution and soluble precipitate; solution in  $H_2SO_4$ , dark violet-brown; on diluting, brown precipitate.

*Application.*—Pluto brown R is dyed on cotton in a feebly alkaline salt bath, and yields a handsome reddish-brown moderately fast to light, fairly fast to washing, and not sensitive to acids or alkalis. A full red-brown shade of good fastness to washing is produced by coupling with diazotised *p* nitraniline. Unions and satins are dyed by the usual methods.

**PLUTO BROWN G G and N B** (Bayer) are similar to Pluto brown R, and yield more yellowish or less reddish shades respectively.

**CHLORAMINE BROWN G** (Bayer).

Reddish-brown powder; aqueous solution, red-brown; HCl, soluble red-brown precipitate; NaOH, soluble yellowish-brown precipitate; solution in  $H_2SO_4$ , green; on diluting, at first blue, then violet, and finally brown precipitate.

*Application.*—Chloramine brown G is dyed on cotton to best advantage in a neutral salt bath, and yields colours of very good fastness to light, acids, alkalis, and chlorine, which are also very satisfactory in fastness to soaping. It dyes shades from flesh colour to yellowish-brown, and may also be applied very well in the padding machine. It is also useful for unions and satins, colouring chiefly the cotton in such goods.

**BENZO CHROME BROWN 5 G, G, R, C R, 3 R, B** (Bayer).

*Benzo Chrome Brown 5 G and G.*—Brown powder; aqueous solution, dark brown; HCl, brown precipitate; NaOH, redder solution and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, brown precipitate.

*Benzo Chrome Brown C R.*—Dark powder; aqueous solution, maroon; HCl, brighter solution; NaOH, redder solution; solution in  $H_2SO_4$ , reddish-blue; on diluting, maroon coloured solution and flocculent precipitate.

*Benzo Chrome Brown B.*—Dark powder; aqueous solution, dark brown;

\* Kallab and Rudolph, *Journ. Soc. Dyers and Col.*, 1891, p. 19.

HCl, black-green precipitate; NaOH, redder solution and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, black-green precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath. The direct dyes range from a yellowish leather brown to a somewhat violet dark brown; of these, that of the "G" brand is fairly fast to light, whilst those of the other brands are of minor fastness; the fastness to soap, acids, and alkalies of the direct dyes is fairly good. By a treatment with bichromate and copper sulphate the shades are considerably altered and very materially improved in fastness to light, washing, acids, and alkalies. Unions and satins may be dyed by the usual methods, the cotton being dyed more intensely than the wool or silk.

#### **DIAZO BROWN G, V, R EXTRA (Bayer).**

*Diazo Brown G.*—Dark powder; aqueous solution, red-brown; HCl, black-brown precipitate; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , black-green; on diluting, brown precipitate.

*Diazo Brown V.*—Black powder; aqueous solution, brown-violet; HCl, dark violet precipitate; NaOH, soluble red-violet precipitate; solution in  $H_2SO_4$ , blue; on diluting, dark violet precipitate.

*Application.*—Cotton is best dyed in a neutral salt bath. Diazo brown G and V dye direct violet-brown shades of moderate fastness to light and washing, and good fastness to acids and alkalies, which, by diazotising and developing with  $\beta$ -naphthol or *m* toluylene diamine, are converted into full dark brown shades of good fastness to washing. Diazo brown R extra dyes a red sensitive to acids, which, by diazotising and developing with diamine, yields a chestnut-brown, or by developing with soda a fine catch brown of good fastness to washing and alkalies, but not fast to light or acids. The direct dyes may also be coupled with diazotised *p* nitraniline.

#### **BENZO NITROL BROWN G, B, O, R O, 3 R (Bayer).**

*Benzo Nitrol Brown G.*—Dark green powder; aqueous solution, dark red-brown; HCl, dark violet-blue precipitate; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Benzo Nitrol Brown B.*—Dark brown powder; aqueous solution, dull brownish-violet; HCl, yellowish-brown solution and flocculent precipitate; NaOH, similar to HCl; solution in  $H_2SO_4$ , bluish-green; on diluting, yellowish-brown solution and precipitate.

*Application.*—The various brands of Benzo nitrol brown are dyed on cotton in a neutral or feebly alkaline salt bath, and fixed by coupling with diazotised paranitraniline (p. 383). They yield when treated in this way intense brown shades of good fastness to washing, acids, and alkalies; Benzo nitrol brown G, when coupled, is fairly fast to light, the other brands are less fast to light.

#### **CONGO BROWN G and R (Berlin, Levinstein).**

Congo brown G is produced by the action of one molecule of diazotised sulphanilic acid on one molecule of benzidine-azoresorcin salicylic acid (Cloth-orange—Bayer).

Congo brown R is produced analogously by using naphthionic acid instead of sulphanilic acid.

Brown powder; aqueous solution, red; HCl, brown precipitate; NaOH, red colour; solution in  $H_2SO_4$ , red-violet; on diluting, dark red-brown precipitate.

*Application.*—Congo brown is dyed in a neutral bath. Congo brown G yields a yellow shade of brown and "R" a reddish brown shade, which are fairly fast to soap, dilute acids, and alkalies, and moderately fast to light. A treatment with copper sulphate makes the shades darker and very fast to light; it also increases the fastness to washing. On wool and silk Congo brown is fairly fast to light, and very fast to washing, milling, stoving, acids, and

alkalies, and becomes also very fast to light by treatment with copper sulphate. Unions are dyed solid brown shades. On satins the silk is dyed more yellowish than the cotton.

**COLUMBIA BROWN R** (Berlin).

Brown powder; aqueous solution, brown; HCl, brown precipitate; NaOH, little change; solution in  $H_2SO_4$ , blue; on diluting, brown precipitate.

*Application.*—Cotton is dyed, in a neutral or feebly alkaline salt bath, a reddish-brown, fairly fast to light and washing and not sensitive to acids or alkalies. By diazotising and developing with *m* toluylene diamine a full dark brown of good fastness to washing is produced. When dyed on unions or satins, Columbia brown dyes the cotton deeper than the animal fibre; it may be used with advantage for mixed goods.

**CHROMANIL BROWN G G and R** (Berlin).

Black powder (G G) or dull brown powder (R); aqueous solution, brown; HCl, brown precipitate; NaOH, redder solution and soluble precipitate; solution in  $H_2SO_4$ , brown; on diluting, brown precipitate.

*Application.*—Chromanil brown is dyed on cotton in a neutral or feebly alkaline salt bath, and yields brown shades which become very valuable by a treatment with bichromate and copper sulphate. Chromanil brown 2 G thus treated yields a fine yellowish-brown, and the "R" brand a reddish-brown of very good fastness to light, washing, acids, and alkalies. Coupling with diazotised *p* nitraniline, with the addition of copper sulphate (p. 383), is also recommended for these dyestuffs.

**ZAMBESI BROWN 2 G and G** (Berlin).

*Zambesi Brown 2 G.*—Grey-violet powder; aqueous solution, red-violet; HCl, soluble brown violet precipitate; NaOH, little change; solution in  $H_2SO_4$ , blue; on diluting, red-violet solution and precipitate.

*Application.*—The various brands of Zambesi brown are dyed on cotton in a neutral or feebly alkaline salt bath, and fixed by diazotising and developing with diamine. Zambesi brown 2 G dyes an intense yellowish-brown, the brand "G" a less yellowish-brown of good fastness to washing, acids, and alkalies, and moderately fast to light; "2 G" is slightly faster to light than "G," and is slightly reddened by alkalies. When dyed on unions or satins, Zambesi brown dyes the cotton a deeper shade than the wool or silk.

**HESSIAN BROWN 2 B N and 2 M** (Leonhardt).

*Hessian Brown 2 B N.*—Benzidine  $\left\{ \begin{array}{l} \text{resorcinazosulphanilic acid.} \\ \text{resorcinazosulphanilic acid.} \end{array} \right.$

Hessian brown 2 B N is produced by the action of one molecule of tetrazodiphenyl on two molecules of resorcinazosulphanilic acid, a yellow azo-dyestuff known as Chrysoin, Tropaeolin R, &c.

Hessian brown 2 M is the corresponding tolidine-compound.

Both show the following reactions:—

Dark brown powder; aqueous solution, brown; HCl, brown precipitate; NaOH, dark red colour; solution in  $H_2SO_4$ , violet-black; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath. The brand 2 B N yields a reddish-brown, and "2 M" a more bluish shade of brown moderately fast to light, fairly fast to washing, and not sensitive to acids or alkalies. The fastness to light is materially improved by a treatment with copper sulphate.

**PEGU BROWN G and R** (Leonhardt).

Dark powder; aqueous solution, brown; HCl, soluble dark brown precipitate; NaOH, similar to HCl; solution in  $H_2SO_4$ , brown-violet; on diluting, brown.



*Application.*—Pegu brown dyes fine catch shades on the various fibres; those of the "R" brand are considerably redder than those of "G" Cotton is dyed in a feebly alkaline or neutral salt bath; the colours possess fairly good fastness to washing and light, and are not sensitive to acids or alkalies. On wool and silk the fastness to light, washing, milling, acids, and alkalies is very good. Unions and satins are dyed by the usual methods. Both kinds of fibres are dyed to the same depth, but wool and silk slightly redder than the cotton.

**DIRECT BROWN 000** (Leonhardt).

Brown powder; aqueous solution, brown-orange; HCl, dark brown precipitate; NaOH, soluble orange-brown precipitate; solution in  $H_2SO_4$ , dark violet; on diluting, dark brown precipitate.

*Application.*—Direct brown 000 is dyed on cotton in a neutral or feebly alkaline salt bath, and yields brown shades of moderately good fastness, which, in combination with other dyestuffs, are useful for the production of cheap browns and olives.

**MIKADO BROWN B, 3 G O, and M** (Leonhardt, Berlin, Bayer).

These dyestuffs are produced, like the other Mikado colours, by the action of alkalies on paranitrotoluene sulphonic acid in the presence of oxidisable substances. The constitution of the products is not known. (See, however, *Mikado yellow* p. 406.) The various brands show the following reactions:—

Dark brown powder; aqueous solution, brown; HCl, brown precipitate; NaOH, no change; solution in  $H_2SO_4$ , violet-black; on diluting, brown precipitate.

*Application.*—Same as Mikado orange; a very large amount of salt is required to exhaust the bath well. The Mikado browns yield various shades of brown, from yellowish- to bluish-brown, which are very satisfactory to washing and not sensitive to acids and alkalies; they are not very fast to light or chlorine.

**DIAMINE BROWN M** (Cassella).

Benzidine  $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{gamma-aminonaphthol sulphonic acid} \\ \text{(combined in alkaline solution).} \end{array} \right.$

Brown powder; aqueous solution, red-brown; HCl, brown precipitate; NaOH, redder solution; solution in  $H_2SO_4$ , violet; on diluting, brown solution and precipitate.

*Application.*—Diamine brown M dyes on cotton in a feebly alkaline or neutral salt bath, a fine reddish chestnut-brown of fairly good fastness to light and washing, and not sensitive to acids or alkalies. The shade becomes deeper and much faster to light and washing by a treatment with copper sulphate alone or in combination with bichromate, whilst a treatment with bichromate alone, or one with chromium fluoride, increases materially the fastness to washing without altering the shade. Diazotising and developing with  $\beta$ -naphthol produces a dark violet-brown, with diamine a deep bluish-brown of very good fastness to washing. On wool and silk handsome browns of good fastness are produced, which become very fast to light by a treatment with copper sulphate. A treatment of the dye on wool with bichromate makes it fast to milling, and on silk the dye becomes fast to milling, and to the water test by a treatment with chromium fluoride. Unions and satins are dyed by the usual methods; Diamine brown M dyes the cotton deeper and slightly more bluish-brown than wool or silk.

**DIAMINE BROWN MR** (Cassella) is similar to Diamine brown M, and yields very valuable brown shades when coupled with diazotised *p* nitraniline (Nitrazol C).

**DIAMINE BROWN B** (Cassella).

Benzidine < salicylic acid.  
phenyl aminonaphthol sulphonic acid.

Dark brown powder; aqueous solution, dark brown; HCl, claret-brown precipitate; NaOH, redder solution; solution in H<sub>2</sub>SO<sub>4</sub>, violet; on diluting, brown solution and precipitate.

*Application and Properties.*—Same as Diamine brown M, the dyestuff, however, is not diazotisable. The shade of Diamine brown B is much more bluish and deeper than that of the "M" brands.

**DIAMINE BROWN V** (Cassella).

Benzidine < gamma-aminonaphthol sulphonic acid.  
metaphenylene diamine.

Brownish-black powder; aqueous solution, reddish-brown; HCl, reddish-violet precipitate; NaOH, soluble reddish-violet precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, blue-violet; on diluting, brown precipitate.

*Application.*—Diamine brown V is dyed on cotton in a feebly alkaline salt bath, and yields violet-brown shades which are fairly fast to light and washing, and fast to acids and alkalis. Colours very fast to washing are obtained by diazotising and developing, or by coupling with diazotised parani-traniline (Nitrazol C).  $\beta$ -naphthol produces a deep violet-brown, diamine a full bluish-brown, and Nitrazol C a very deep maroon-brown. Unions and satins may be dyed by the usual methods, the cotton being dyed a deeper and slightly more violet shade than wool or silk.

**DIAMINE BROWN S** (Cassella) possesses the same properties and reactions as Diamine brown V, but is more soluble.

**DIAMINE BROWN 3 G** (Cassella).

Brown powder; aqueous solution, yellowish-brown; HCl, yellowish-brown precipitate; NaOH, redder solution; solution in H<sub>2</sub>SO<sub>4</sub>, brown-red; on diluting, brown solution and precipitate.

*Application.*—Diamine brown 3 G is dyed on cotton in a feebly alkaline salt bath, and yields yellowish-brown shades of fairly good fastness to light and washing, which are not sensitive to acids, and are only slightly reddened by alkalis. The colour becomes very fast to light by a treatment with copper sulphate. On wool and silk yellowish-brown shades of good fastness are produced, which also become very fast to light by a treatment with copper sulphate. On unions and satins solid shades of yellowish-brown are produced by the usual methods.

**DIAMINE CATECHIN B, G, and 3 G** (Cassella).

Dark powder; aqueous solution, brown; HCl, brown precipitate; NaOH, slightly redder solution; solution in H<sub>2</sub>SO<sub>4</sub>, violet; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a feebly alkaline or neutral salt bath. Diamine catechin G dyes yellowish catch shades, the "3 G" brand more yellowish-brown, and "B" violet-brown shades of fairly good fastness to light and washing. Diamine catechin B is the best of the three colours in fastness to light and also to hot pressing, and is very useful, both for browns and for compound shades; this applies also to "3 G," whereas G is chiefly used for catch browns. By a treatment with copper sulphate and bichromate the fastness to washing becomes very good without the shades being altered. Unions are dyed by the usual methods, the cotton being coloured deeper and slightly more bluish than the wool.

**DIAMINERAL BROWN G** (Cassella).

Brown powder; aqueous solution, reddish-brown; HCl, brown precipitate; NaOH, redder solution and soluble precipitate; solution in  $H_2SO_4$ , dark reddish-blue; on diluting, brown precipitate.

*Application.*—Cotton is best dyed in a neutral salt bath, and then treated with copper sulphate and bichromate. Diamineral brown thus yields a reddish-brown of very good fastness to light, washing, acids, and alkalis. The direct shade is also fairly fast, but darkened by alkalis. Unions and satins are dyed by the one-bath methods.

**OXYDIAMINE BROWN G, 3 GN, RN** (Cassella).

Brown powder; aqueous solution, orange-brown or reddish-brown; HCl, brown precipitate; NaOH, soluble orange-brown precipitate; solution in  $H_2SO_4$ , maroon or violet; on diluting, brown precipitate.

*Application.*—Oxydiamine brown is dyed on cotton in a neutral or feebly alkaline bath fairly fast to washing, moderately fast to light, and good to acids and alkalis. The brands G and 3 GN dye yellowish-browns. Oxydiamine brown RN dyes a reddish-brown, which may be deepened and improved in fastness to washing by a treatment with diazotised *p* nitraniline. Unions and satins may be dyed by the one-bath methods; Oxydiamine brown G and 3 GN yield fairly solid shades, whereas "RN" dyes the cotton much deeper than the wool.

**DIAMINE BRONZE G** (Cassella).

Tolidine  $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{amidonaphthol disulphonic acid II—phenylene diamine.} \end{array} \right.$

Dark powder; aqueous solution, brown; HCl, brown precipitate; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , violet-blue; on diluting, brown precipitate.

*Application.*—Cotton is best dyed in a neutral salt bath. Bronze brown and olive shades of fairly good fastness to light, washing, and acids, and not sensitive to alkalis, are obtained. A treatment with chromium fluoride makes the colour very fast to washing without altering the shade. Copper sulphate makes the colour browner, and also very fast to washing. Olives very fast to washing are produced by coupling with diazotised *p* nitraniline (Nitrazol C). Unions and satins are dyed by the usual methods. The cotton is dyed a deeper shade than wool or silk.

**DIAMINE CUTCH** (Cassella).

1 : 5 Naphthylene diamine 3 : 7 sulphonic acid  $\left\{ \begin{array}{l} \alpha\text{-naphthylamine.} \\ \alpha\text{-naphthylamine.} \end{array} \right.$

Brown powder; aqueous solution, claret-red; HCl, blue precipitate; NaOH, soluble red precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Application.*—Diamine cutch is dyed on cotton and silk by the diazotising and developing process. The direct shades are of no value. It is dyed on cotton in a feebly alkaline salt bath. Diazotising and developing with a warm solution of soda produces a handsome cutch brown, very fast to washing, moderately fast to light, and not sensitive to acids or alkalis, also fairly fast to chlorine. Aminodiphenylamine yields a darker and more bluish-brown of good fastness to washing, acids, and alkalis, and fairly good fastness to light. Silk is dyed in acidulated boiled-off liquor or with acetic acid, diazotised, and developed. Developing with soda yields a reddish-brown, sulphuric acid a more yellowish-brown, and aminodiphenylamine a full bluish-brown of very good fastness to washing and water.

**DIAMINE NITRAZOL BROWN B, B D, R D, G, T** (Cassella).

Brown or dark brown powder; aqueous solution, brown; HCl, brown pre-

cipitate; NaOH, little change; solution in  $H_2SO_4$ , dark red (G and B), or violet (R D and T), or olive-black (B D); on diluting, brown precipitate.

*Application.*—The Diamine nitrazol browns are chiefly used for dyeing cotton by the coupling process. The brands R D, B D, and T, however, are also dyed direct. The coupled colours are very fast to washing, acids, alkalies, and cross-dyeing, and moderately fast to light. They yield very intense browns, of which that of G is the yellowest, R D the reddest, B and B D more bluish, and T the darkest, as also the best in fastness to cross-dyeing. Diamine nitrazol brown G is used for dyeing unions. In a cold bath it dyes almost exclusively the cotton, and hardly stains the wool. On silk the coupled colours are very fast to soap and water.

**DIANIL BROWN B D, B, and D (M.L.B.).**

*Dianil Brown B D.*—Black powder; aqueous solution, dark brown; HCl, brown precipitate; NaOH, little change; solution in  $H_2SO_4$ , dark blue-violet; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath. Dianil brown B D yields a full bluish shade of brown, moderately fast to light, fairly fast to washing, and good to acids and alkalies. The "B" brand dyes bluer shades of brown, and "D" still bluer and darker browns, which are slightly faster to light, and resemble in other respects Dianil brown B D. By coupling with diazotised paranitraniline (Azophor red P N), deeper browns of very good fastness to washing are produced. Unions and satins are dyed by the one-bath method, the cotton being dyed deeper than wool or silk.

**DIANIL BROWN 3 G O, 5 G, 2 G, A, R, 2 R (M.L.B.).**

*Dianil Brown 3 G O.*—Brown powder; aqueous solution, orange-brown; HCl, brown precipitate; NaOH, soluble orange-brown precipitate; solution in  $H_2SO_4$ , violet; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath various shades of brown, which are fairly fast to washing, moderately fast to light, and good to acids and alkalies. A treatment with diazotised paranitraniline improves the fastness to washing. Unions and satins may be dyed fairly solid by the one-bath methods.

**DIANIL JAPONIN G (M.L.B.).**

Brown powder; aqueous solution, brown; HCl, brown precipitate; NaOH, redder solution and soluble precipitate; solution in  $H_2SO_4$ , dark violet; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath good yellowish catch shades, which are fairly fast to washing, moderately fast to light, and good to acids and alkalies. By a treatment with copper sulphate the fastness to light is improved, and by treatment with a mixture of copper sulphate and bichromate the fastness to washing. The colour may also be coupled on the fibre with diazotised *p* nitraniline. Unions and satins are dyed by the one-bath methods.

**TRIAZOL BROWN GOO (Oehler-Griesheim).**

Brown powder; aqueous solution, orange-brown; HCl, reddish-brown precipitate; NaOH, soluble orange-brown precipitate; solution in  $H_2SO_4$ , violet; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath a yellowish shade of brown, fairly fast to washing, moderately fast to light, and good to acids and alkalies.

**ALKALI BROWN R (Dahl). BENZO BROWN 5 R (Bayer). COTTON BROWN R (B.A.S.F.).**

Azo-dyestuff made by combining diazotised Primuline or dehydrothio *p* toluidine sulphonic acid with *m* phenylene diamine.

Chocolate brown powder; aqueous solution, dark red-brown; HCl, brown precipitate; NaOH, redder solution and soluble brown precipitate; solution in  $H_2SO_4$ , dark violet (Alkali brown) or red-brown (Benzo or Cotton brown); on diluting, brown precipitate.

*Application.*—These very similar or identical dyestuffs are dyed on cotton in a neutral or feebly alkaline salt bath, and yield bright red-brown shades of moderate fastness to light, fairly good fastness to washing, and not sensitive to acids or alkalis. Unions may be dyed by the usual methods.

**ALKALI DARK BROWN G, V. ALKALI RED-BROWN 3 R, 2 R, T (Dahl).**

These dyestuffs are mixed diazo-compounds of benzidine, &c., with one molecule of the bisulphite derivative of nitroso  $\beta$ -naphthol, and one molecule of an aminonaphthol sulphonic acid.

*Alkali Dark Brown G and V.*—Dark brown powder; aqueous solution, dark violet (V) or violet-red (G); HCl, dark precipitate and violet solution; NaOH, soluble violet-brown (V) or reddish (G) precipitate; solution in  $H_2SO_4$ , blue; on diluting, brown precipitate.

*Alkali Red-brown* possesses similar reactions.

*Application.*—These dyestuffs are chiefly dyed on cotton in a feebly alkaline salt bath, and yield red-brown or dark violet-brown shades, which are fairly fast to washing, not sensitive to acids or alkalis, and not very fast to light. Alkali dark brown V may be diazotised and developed with  $\beta$ -naphthol or diamine and thus yield dark brown shades of good fastness to washing. Its treatment with bichromate and copper sulphate the shade becomes yellower, and is improved in fastness to washing, but not to light. Unions are dyed with these dyestuffs by the usual methods.

**NAPHTHAMINE BROWN (Kalle).**

*Naphthamine Brown 4 G.*—Brown powder; aqueous solution, reddish-brown; HCl, brown precipitate; NaOH, redder solution; solution in  $H_2SO_4$ , violet; on diluting, brown precipitate.

*Naphthamine Brown 2 B.*—Blackish-green powder; aqueous solution, dark brown; HCl, brown precipitate; NaOH, redder solution; solution in  $H_2SO_4$ , violet; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath. The various brands of Naphthamine brown, such as 2 G, 4 G, D 5 G, R E, B, and 2 B, yield yellowish, reddish, or bluish shades of brown, which are fairly fast to washing, acids, and alkalis, and may be improved in fastness to washing by a treatment with bichromate. Naphthamine brown 4 G is sensitive to alkali. The "R E" brand may be coupled with diazotised paranitraniline, the shade thereby becoming more intense, yellower, and faster to washing. Unions and satins may be dyed fairly solid by the general methods.

**TERRA COTTA F (Geigy).**

Primuline  
Naphthionic acid  $\text{>}$  *m* phenylene diamine.

Chocolate brown powder; aqueous solution, yellowish-brown; HCl, brown precipitate; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , brown; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath a reddish-brown (terra-cotta) shade, which is fairly fast to washing, acids, and alkalis, and moderately fast to light.

**POLYCHROMIN B. FAST COTTON BROWN R. DIRECT BROWN R (Geigy).**

This dyestuff, produced by boiling equal molecular weights of paranitrotoluene sulphonic acid and paraphenylene diamine with caustic soda, is probably an azo-compound.

**Brown powder**; aqueous solution, dark brown; HCl, blue-black precipitate; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , dark violet-red; on diluting, blue-black precipitate.

*Application.*—Cotton is dyed in a neutral salt bath, which is not exhausted very well. A red-brown shade is obtained which is moderately fast to light and washing, and becomes darker by acids, but is not sensitive to alkalis. Diazotising and developing with  $\beta$ -naphthol yields a claret-red and with *m* toluylene diamine a brown, fast to washing, acids, and alkalis; resorcin yields also claret and  $\alpha$ -naphthol brown-red not fast to alkalis, but fast to washing.

#### DIPHENYL FAST BROWN G (Geigy).

Product of the diazotisation of nitrosostilbene disulphonic acid-azo-aniline, and combination with phenylamidonaphthol sulphonic acid  $\gamma$ .

Dark brown powder; aqueous solution, dark yellowish-brown; HCl, blackish-brown precipitate; NaOH, dark brown precipitate; solution in  $H_2SO_4$ , dark blue; on diluting, blackish-brown precipitate.

*Application.*—Cotton is dyed in a neutral salt bath yellowish-brown shades, fairly fast to washing and moderately fast to light, and not sensitive to acids or alkalis. Unions and satins are dyed by the usual methods, the cotton coming out deeper, but the same tone as the wool.

DIPHENYL FAST BROWN G N (Geigy) is a more recent brand of similar properties.

DIPHENYL CATECHINE G (Geigy) is similar in chemical composition, reactions, and properties to the preceding brands, but dyes less handsome catch shades.

#### DIPHENYL BROWN (Geigy).

*Diphenyl Brown R N.*—Benzidine  $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{methyaminonaphthol sulphonic acid } \gamma. \end{array} \right.$

Black powder; aqueous solution, dark brown; HCl, dark red-brown precipitate; NaOH, no change; solution in  $H_2SO_4$ , violet; on diluting, brown precipitate.

*Application.*—Cotton is dyed by the various brands of Diphenyl brown, such as R N, B N, G N, G T, R V, conc., various shades of brown of fairly good fastness to light and washing, and good fastness to acids and alkalis. A treatment with bichromate and copper sulphate greatly increases the fastness to light and washing. Unions and satins, and also wool and silk, are dyed by the usual methods.

DIPHENYL RED BROWN G (Geigy) is similar to the preceding, and dyes a bright reddish-brown, which becomes yellower by a treatment with bichromate and copper sulphate.

#### CHLORANTINE BROWN R (Chem. Ind. Basle).

Brownish powder; aqueous solution, dark red-brown; HCl, solution much yellower and soluble precipitate; NaOH, no change; solution in  $H_2SO_4$ , violet-black; on diluting, at first black, then brown, and finally brown precipitate.

*Application.*—Cotton is dyed, in a feebly alkaline or neutral salt bath, a bright red-brown shade of very good fastness to light and washing, acids and chlorine, which becomes browner (less reddish) by the action of alkalis. Unions and satins are dyed by the usual methods, the dyestuff chiefly dyeing the cotton.

#### CUPRANIL BROWN B, R, G (Chem. Ind. Basle).

*Cupranil Brown R.*—Chocolate-brown powder; aqueous solution, dark red-brown; HCl, dark brown precipitate; NaOH, slightly redder solution; solution in  $H_2SO_4$ , violet; on diluting, dark brown precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath with the

various brands of Cupranil brown, which yield bluish, reddish, or yellowish shades respectively of brown. The colours are fairly fast to light and washing, and not sensitive to acids or alkalis. Treatment with copper sulphate greatly improves the fastness to light and washing, especially that of the "B" brand, whereas "R" and "G" should be soaped after coppering, in order to yield the best fastness to washing. Unions and satins may be dyed by the usual methods.

#### TRISULPHONE BROWN B, G, G G (Sandoz).

Benzidine  $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{amidonaphthol sulphonic acid—}m \text{ diamine.} \end{array} \right.$

The Trisulphone browns are said to be constituted according to the above general scheme.

*Trisulphone Brown B.*—Greyish-brown powder; aqueous solution, brown; HCl, blackish-brown precipitate; NaOH, reddish-brown solution; solution in  $\text{H}_2\text{SO}_4$ , bluish-violet; on diluting, dark brown precipitate.

*Trisulphone Brown G and G G* show similar, but more yellowish reactions.

*Application.*—Cotton is dyed in a feebly alkaline salt bath, and may be treated with bichromate and copper sulphate without the shade being much altered. Trisulphone brown B yields a handsome chestnut-brown, the brands "G" and "G G" more yellowish-browns. The direct dyes are moderately fast to light, and fairly fast to washing, and not sensitive to acids or alkalis; the after-treatment improves the fastness. Unions and satins may be dyed by the usual methods, the animal fibre coming out more yellowish than the cotton.

#### TITAN BROWN O, R, Y (Holliday).

*Titan Brown R.*—Brown powder; aqueous solution, dark brown; HCl, brown precipitate; NaOH, no change; solution in  $\text{H}_2\text{SO}_4$ , dark red; on diluting, brown precipitate.

*Application.*—Titan brown is dyed on cotton in a neutral salt bath, and yields shades of brown, which are moderately fast to washing, not very fast to light, and, with the exception of the "O" brand, reddened by acids and alkalis. Wool and silk, and also unions and satins, may be dyed by the usual methods.

#### CHLORAZOL BROWN A, B, C, N, R (Holliday).

*Chlorazol Brown A.*—Brown powder; aqueous solution, dark brown; HCl, no change; NaOH, dull crimson solution; solution in  $\text{H}_2\text{SO}_4$ , terra cotta; on diluting, brown.

*Application.*—The Chlorazol browns are dyed on cotton in a neutral salt bath, and yield various shades of brown, moderately fast to washing, not very fast to light, not sensitive to acids, but reddened by alkalis. Treatments with bichromate and copper sulphate increase the fastness to light and washing. The Chlorazol browns are not important for the dyeing of the animal fibres.

#### PARAMINE BROWN and PARAMINE DARK BROWN (Claus & Co.).

*Paramine Brown R and C.*—Brown powder; aqueous solution, brown; HCl, brown precipitate; NaOH, red solution; solution in  $\text{H}_2\text{SO}_4$ , violet; on diluting, brown precipitate.

*Paramine Dark Brown N* gives similar, slightly bluer, reactions.

*Paramine Dark Brown V.*—Black powder; aqueous solution, violet; HCl, violet precipitate; NaOH, soluble crimson precipitate; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, violet precipitate.

*Application.*—These dyestuffs are dyed on cotton in a feebly alkaline salt bath, and yield brown shades fairly fast to washing, moderate to light, and not sensitive to acids or alkalis. Paramine brown C dyes a handsome catch shade, "R" a more bluish-brown, which are considerably improved in

fastness to light and washing without much alteration of shade by a treatment with bichromate and copper sulphate. The Paramine dark browns dye dark shades of brown which well serve for saddening.

**DIAMINE BLACK B H** (Cassella).

Benzidine  $\left\{ \begin{array}{l} \gamma\text{-aminonaphthol sulphonic acid.} \\ \text{aminonaphthol disulphonic acid H.} \end{array} \right.$

Greyish-blue powder; aqueous solution, reddish-blue; HCl, violet precipitate; NaOH, red-violet; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, violet precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath pale blue to dark navy blue shades, which are fairly fast to light and soaping, and very good to acids and alkalis. The dyestuff is readily soluble, and used as a self-colour and for all kinds of mixed shades on all sorts of cotton materials, and also in dyeing machines. By diazotising and developing the fastness to washing becomes very good. Beta-naphthol produces intense navy blues, whilst with diamine jet blacks and with resorcin greenish-blacks are obtained. By mixing these three developers a great variety of blacks fast to washing may be dyed. Other developers, such as Fast blue developer A D or naphthylamine ether, also yield good navies.

Unions and satins may be dyed by the one-bath method in combination with dyestuffs colouring the wool or silk, since Diamine black B H dyes almost exclusively the cotton. The dyestuff, therefore, finds much application for staining the cotton in unions, the wool of which has been acid dyed, and in satins, the silk of which is to be dyed subsequently with acid or basic dyestuffs. Diamine black B H may be fixed also on these fibres by diazotising and developing for the production of colours fast to washing. Silk may be dyed in a slightly acid bath, with subsequent diazotising and developing in order to produce very fast blacks.

**DIAMINE BLACK R O** (Cassella).

Benzidine  $\left\{ \begin{array}{l} \text{gamma-aminonaphthol sulphonic acid.} \\ \text{gamma-aminonaphthol sulphonic acid} \\ \text{(combined in alkaline solution).} \end{array} \right.$

Black powder; aqueous solution, violet-black; HCl, blue precipitate; NaOH, violet colour; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, red-blue precipitate.

*Application and Properties.*—Diamine black R O is very similar to Diamine black B H, and is applied in the same way. It is more reddish and less bright in shade, and not so readily soluble, but still superior in fastness to light and washing.

**DIAMINE BLACK B O** (Cassella) is the ethoxybenzidine compound corresponding to Diamine black R O, and strongly resembles the same in reactions and tinctorial properties, but is more bluish in shade.

**DIAMINE BLACK H W** (Cassella).

Product of the combination of 1 molecule Diamine black B H (see above) with 1 molecule diazotised paranitraniline.

Dark grey powder; aqueous solution, black-blue; HCl, blue precipitate; NaOH, no change; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, blue precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath greenish-black shades, fairly fast to light and washing, and fast to acids and alkalis. This brand is not suitable for the diazotising process. Unions and satins are dyed by the one-bath method. Unions are dyed solid shades; in satins the cotton is dyed deeper than the silk.



**OXYDIAMINE BLACK** (Cassella).

A great number of brands are found in commerce which show about the same general reactions.

Greyish to black powders; aqueous solution, violet-black or bluish-black; HCl, dark precipitates; NaOH, dark soluble precipitates; solution in  $H_2SO_4$ , blue-black or violet-black; on diluting, dark precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath full shades of reddish, bluish, or jet-blacks, which are fairly fast to washing and good to acids and alkalies. The fastness to light varies, some are moderately fast to light, other brands less, and some possess a fairly good fastness to light. Coupling of the brands A, J W, J E, &c., with diazotised paranitraniline gives blacks very fast to washing, acids, and alkalies, and also to cross-dyeing; the shade may be brightened by topping in the coupling bath with a slight amount of New methylene blue. A treatment of the direct black with formaldehyde also improves the fastness to washing. Unions and satins are dyed by the one-bath method; the cotton is dyed full shades of black, whereas silk and wool remain lighter in colour, and may be brought to shade by the addition of neutral dyeing wool blacks, such as Naphthylamine black 4 B, or by subsequent dyeing of the animal fibre.

**PARADIAMINE BLACK B, BB, FFB** (Cassella).

Dark powder; aqueous solution, bluish-black; HCl, bluish-black precipitate; NaOH, dark soluble precipitate; solution in  $H_2SO_4$ , dark greenish-blue; on diluting, dark precipitate.

*Application and Properties.*—Like Oxydiamine black. These dyestuffs resemble the preceding very much, and are distinguished by fulness of shade and exceedingly good fastness to acids, which makes them suitable for dyeing cotton warps in unions to be cross-dyed.

**DIAMINE JET BLACK SS, O O, R B, Cr** (Cassella).

Grey powder; aqueous solution, violet-black; HCl, dark blue ("SS" and "O O" brands) or violet-black ("R B" and "Cr" brands) precipitate; NaOH, solution redder and soluble precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath deep shades of black similar to Oxydiamine black, but greatly superior in fastness to light and very satisfactory in fastness to washing; the fastness to acids and alkalies is good. A light treatment with bichromate fixes the colours very fast to washing; deep shades are boiled ten to fifteen minutes with 3 per cent. bichromate and 2 to 3 per cent. acetic acid. Diamine jet black SS and O O yield good blacks when diazotised and developed with *m* toluylene diamine and resorcin. Very good dark browns are produced by coupling the various brands of Diamine jet black with diazotised paranitraniline.

**DIAMINERAL BLACK B, 3 B, 6 B** (Cassella).

Grey or dark blue powder; aqueous solution, blue-black or violet-black; HCl, black precipitate; NaOH, redder solution and soluble dark precipitate; solution in  $H_2SO_4$ , blue; on diluting, dark precipitate. \*

*Application.*—Diamineral black is dyed on cotton in a feebly alkaline salt bath, and yields reddish- to bluish-blacks and deep navies ("6 B"), which, when treated with bichromate and copper sulphate, are very fast to light, washing, acids, and alkalies.

**DIAMINOGENE** (Cassella).

Polyazo-dyestuff produced with acetylnaphthylendiamine sulphonic acid and  $\gamma$ -aminonaphthol sulphonic acid.

Various brands of Diaminogene, such as Diaminogene extra, R, B R, B W, and C C L, are in the market, which show the following general reactions:—

Bluish-grey powder; aqueous solution, reddish-blue; HCl, blue or violet

precipitate; NaOH, dark soluble precipitate and redder solution; solution in  $H_2SO_4$ , blue; on diluting, blue or violet precipitate.

*Application.*—Cotton is dyed with Diaminogene in a feebly alkaline salt bath grey to dark blue shades. The fastness of the direct dyes to light, acids, and alkalis is very good; the fastness to washing, however, is satisfactory only for greys. By diazotising and developing on the fibre, colours very fast to washing and also to light, acids, and alkalis are produced. Developing with *m* toluylene diamine yields excellent jet blacks,  $\beta$ -naphthol very good navies, and resorcin dark green; these three developers may be mixed with each other for the production of a variety of fine black shades. Indigo-blue shades are produced with  $\gamma$ -aminonaphthol sulphonic acid, aminodiphenylamine or naphthylamine ether. Coupling with diazotised paranitraniline produces a greenish-grey very fast to soaping.

Wool is dyed with advantage in a neutral or feebly acid bath with Diaminogene extra, bluish-grey to dark blue shades very fast to light and washing being obtained.

Silk is dyed in acidulated boiled-off liquor; if the colour is diazotised and developed as indicated for cotton, excellent blacks and navies are produced very fast to light, washing, water, acids, and alkalis.

Unions are dyed by the one-bath method, especially with Diaminogene B which gives solid shades of dark blue on this material, whereas Diaminogene extra is used to colour the wool deeper than the cotton.

Satins are also dyed by the one-bath method in a soap bath, the cotton being then dyed deeper shades of deep blue than the cotton. The colours may also be diazotised on satin, Diaminogene extra yielding blue-blacks, and Diaminogene B deep blacks by developing with  $\beta$ -naphthol and diamine.

#### OXYDIAMINOGENE (Cassella).

A number of various brands—*e.g.*, OB, OT, ED, FN, &c.—are in the market, which are also principally applied by the diazotising and developing method on cotton, and yield blacks and dark blues of very good fastness to light, washing, acids, and alkalis.

#### BENZO FAST GREY and BENZO FAST BLACK (Bayer).

Dark grey or black powder; aqueous solution, violet-black; HCl, dark violet precipitate; NaOH, makes the solution slightly bluer; solution in  $H_2SO_4$ , black-green; on diluting, dark violet solution and precipitate.

*Application.*—Benzo fast grey and Benzo fast black dye on cotton in alkaline baths very good greys and blacks fairly fast to light and washing, and good to acids and alkalis. Benzo fast black levels well and may be used with advantage, as a saddening colour for mixed shades. It may also be diazotised and developed on the fibre to produce good blacks, which possess a very satisfactory fastness to washing.

#### DIRECT DEEP BLACK (Bayer).

*Direct Deep Black R W.*—Grey powder; aqueous solution, reddish-black; HCl, black precipitate; NaOH, dark soluble precipitate and blue solution; solution in  $H_2SO_4$ , dark blue-violet; on diluting, dark precipitate.

*Application.*—A great number of brands of Direct deep black—*e.g.*, R W, E W, E, EB, B, G, T—are in the market, which are chiefly used on cotton and union goods.

Cotton is dyed in a feebly alkaline salt bath deep shades of black, which are fairly fast to washing and acids and good to alkalis, but not very fast to light. They are employed in great quantities for blacks on all kinds of cheap cotton goods. By coupling with diazotised paranitraniline, blacks very fast to washing and alkalis are produced, the shade of which may be brightened by an addition of a little Methylene blue to the coupling bath. The direct dye may also be greatly improved by a treatment with formaldehyde (p. 385).

Unions are dyed by the one-bath method, the cotton being dyed a deeper shade than the wool, which may be shaded by neutral dyeing wool blacks. Satins may also be dyed by the one-bath method.

**DIRECT BLUE-BLACK N, B, and 2 B (Bayer).**

*Direct Blue-Black B.*—Black powder: aqueous solution, violet-black; HCl, blue-black precipitate; NaOH, little change; solution in  $H_2SO_4$ , blue-black; on diluting, blue-black precipitate.

*Application and Properties.*—Like Direct deep black. The shades are more bluish-black, that of 2 B is the bluest.

**PLUTO BLACK (Bayer).**

A great number of brands are found in the market, such as A, B, 3 B, F, FF, G, R, CR, SS, BS extra, most of which show the following reactions:—

Grey or black powder; aqueous solution, dark red-violet to almost black; HCl, blue to black precipitate; NaOH, violet, blue, or black soluble precipitate; solution in  $H_2SO_4$ , dark violet, blue, or greenish-blue; on diluting, dark precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath deep shades of black, which, on the whole, resemble those of direct deep black, but are faster to acids. Pluto black BS extra is very fast to acids, and is very well suited to be dyed on cotton-warps worsteds in the milling machine and then to be cross-dyed in an acid bath. Pluto black SS and CR are superior to the other brands owing to their very good fastness to washing and light, and are also good to acids and alkalis. By a treatment with bichromate they are fixed very fast to washing. Unions and satins are dyed by the one-bath methods, the cotton being dyed deeper than the wool or silk.

**BENZO CHROME BLACK B and N (Bayer).**

Black powder; aqueous solution, violet-black; HCl, violet-black precipitate; NaOH, little change; solution in  $H_2SO_4$ , blue; on diluting, blue and dark precipitate.

*Application.*—Benzo chrome black yields on cotton dyed in a feebly alkaline salt bath, navy blues fairly fast to light and washing, and good to acids and alkalis. They find their chief application for very fast blacks which are produced by after-treatments with bichromate and copper sulphate. They are also recommended for satins since, in an alkaline soap bath, they chiefly dye the cotton.

**DIAZO BLACK (Bayer).**

*Diazo Black B.*—Benzidine  $\left\{ \begin{array}{l} \alpha\text{-naphthylamine sulphonie acid L.} \\ \alpha\text{-naphthylamine sulphonie acid L.} \end{array} \right.$

Diazo black is furnished to the trade in a considerable number of brands, such as B, 2 B, 3 B, G, H, R, B H N, &c., which show the following general reactions:—Grey to black powder; aqueous solution, violet to reddish-blue, HCl, blue or violet precipitate; NaOH, violet to blue solution; solution in  $H_2SO_4$ , blue; on diluting, blue or violet precipitate.

*Application.*—When dyed on cotton in a feebly alkaline salt bath, the various brands of Diazo black yield more or less reddish-blues (navies) which are fairly fast to washing, but not very fast to light, and good to acids and alkalis. By diazotising and developing with  $\beta$ -naphthol good navies and blue-blacks, and with *m* toluene diamine jet-blacks are produced which are very fast to washing, acids, and alkalis. Diazo black B H N is the best of this series, both in fastness to light and in purity of shade; it dyes direct good navies, and develops also navies and blacks. A hot treatment of the developed shade in order to enhance the fastness to light with copper sulphate, is especially recommended for Diazo black 3 B. Unions and satins are dyed with

advantage by the one-bath method, especially with Diazo black B H N, which chiefly dyes the cotton, and stains but slightly wool or silk.

**DIAZO BLUE-BLACK** (Bayer) is similar to the Diazo blacks and yields blue-black shades both by direct dyeing and developing.

**DIAZO FAST BLACK G, 3 B, S D** (Bayer).

Grey powder; aqueous solution, blue; HCl, dark precipitate; NaOH, makes the solution redder; solution in  $H_2SO_4$ , greenish-blue; on diluting, dark precipitate.

*Application.*—Like Diazo black. The fastness is about the same, except the fastness to light, which is considerably better than that of the Diazo blacks. The brand 3 B becomes very fast to light by a hot treatment with copper sulphate. Diazo fast black S D dyes direct good grey shades of very satisfactory fastness.

**DIAZO BRILLIANT BLACK B and R** (Bayer).

*Diazo Brilliant Black B.*—Tolidine  $\left\langle \begin{array}{l} \alpha\text{-naphthylamine sulphonic acid L.} \\ \alpha\text{-naphthylamine sulphonic acid L.} \end{array} \right.$

Brownish-black powder; aqueous solution, brown; HCl, blue precipitate; NaOH, soluble violet precipitate; solution in  $H_2SO_4$ , violet; on diluting, blue precipitate.

*Application.*—Diazo brilliant black is dyed in a feebly alkaline salt bath on cotton. The direct shade is a brown-red or dull red-violet without value; by the diazotising process, however, good browns, blues, and blacks are obtained. Treatment of the diazotised dye for five minutes at  $60^\circ C.$  in a 5 per cent. soda solution produces a handsome catch-brown, fast to washing and alkalis, but not to light or acids. Developing with beta-naphthol yields blues; with diamine, blacks, which are good to washing, alkalis, and acids, but not very fast to light.

**DIAZO ETHYL BLACK B and R** (Bayer) are similar to Diazo brilliant black in chemical reactions and tinctorial properties.

**BENZO NITROL BLACK B and T** (Bayer).

Grey powder; aqueous solution, dull violet; HCl, dark precipitate; NaOH, redder ("B") or slightly bluer ("T") solution; solution in  $H_2SO_4$ , greenish-blue ("B") or dull violet ("T"); on diluting, dark precipitate.

*Application.*—Benzo nitrol black is dyed on cotton in a feebly alkaline salt bath, and then coupled on the fibre with diazotised paranitraniline (Benzo-nitrol). It thus yields blue-black ("B") or jet-black ("T"), which are fairly fast to washing, good to acids and alkalis, but not very fast to light.

**NEUTRAL GREY** (Berlin).

Black-brown powder; aqueous solution, black-green; HCl, violet-black precipitate; NaOH, little change; solution in  $H_2SO_4$ , dark bluish-green; on diluting, dark violet precipitate.

*Application.*—Neutral grey is chiefly dyed on cotton for the production of pure slightly reddish shades of grey, which are fairly fast to light and washing, and good to acids and alkalis.

**COLUMBIA BLACK** (Berlin).

Columbia black is brought into commerce in the form of a great number of brands, such as F F, F F extra, F B, F B B, B, R, 2 B X, 2 B W, 3 B, 4 B, E A, W A, which show approximately the following general reactions:—

Grey or black powder; aqueous solution, violet-black; HCl, violet-black or blue-black precipitate; NaOH, dark soluble precipitate; solution in  $H_2SO_4$ , dark blue-violet, blue, or dark greenish-blue; on diluting, dark precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath deep shades of black, which are fairly fast to washing, good to acids and alkalis, but not very fast to light. Columbia black R dyes very reddish, the other brands more

bluish shades of black. Columbia black F F yields a very fine deep shade of black, which is very satisfactory to acids and may be used with advantage for dyeing cotton warps-worsted in the milling machine, with subsequent acid cross-dyeing with acid dyestuffs. Unions and satins may be dyed by the one-bath methods, the cotton being generally dyed deeper shades than the wool or silk. Columbia black B W dyes cotton and wool fairly solid shades.

**CHROMANILE BLACK B F, 2 B F, 3 B F, R F, 2 R F** (Berlin).

Black-brown powder; aqueous solution, reddish-black; HCl, blue precipitate; NaOH, little change; solution in  $H_2SO_4$ , black-blue; on diluting, blue precipitate.

*Application.*—Chromanile black serves chiefly for dyeing cotton, with a subsequent treatment with copper sulphate and bichromate. The direct dyes are dark blues of fairly good fastness to light and washing, and, by an after-treatment, they are converted into blue-blacks and jet-blacks of very good fastness to light and washing. Unions are well dyed in one bath with the "2 B F" brand.

**ZAMBESI BLACK** (Berlin).

A great number of various brands, such as Zambesi black D, F, B, B R, V, 2 G, &c., are found in commerce.

*Zambesi Black D.*—Black-brown powder; aqueous solution, reddish-black; HCl, brown precipitate; NaOH, soluble blue-black precipitate; solution in  $H_2SO_4$ , bluish-green; on diluting, brown precipitate.

*Application.*—The various brands of Zambesi black are chiefly used on cotton and usually fixed on this fibre by the diazotising and developing method. They are dyed in neutral or feebly alkaline salt baths, and thus yield various shades of greys, dark blues, and blacks. Especially the "D" and "V" brands produce good greys and blacks, which are fairly fast to light and washing and good to acids and alkalis. By diazotising and developing very good blacks and navies are produced. Zambesi black D yields a jet-black with *m* toluylene diamine or with a mixture of beta-naphthol and resorcin, a jet black with a bluish shine overhand with Nerogene D (p 383), a black-blue with beta-naphthol, and a dark navy blue with naphthylamine ether. The various developed shades are very fast to washing, acids, and alkalis, and possess a very good resistance to light. Coupling with diazotised paranitraniline may also be applied to the Zambesi blacks, and most of them—*e.g.*, "B," "F," "B R"—may also be treated with copper sulphate, or a mixture of bichromate and copper sulphate, in order to improve the fastness of the direct shades to light and washing.

Unions and satins may be dyed by the one-bath methods, the cotton being generally dyed deeper than wool or silk.

**COTTON BLACK** (B.A.S.F.).

A great number of "Cotton blacks" of this firm—*e.g.*, B N, B G, 3 G, 3 B, R N, &c.—are brought into the market, which show the following general reactions:—

Black powder; aqueous solution, violet-black; HCl, black precipitate; NaOH, little change or red-violet solution; solution in  $H_2SO_4$ , green or greenish-black; on diluting, violet-black precipitate.

*Application.*—The various brands of "Cotton black" are chiefly used on cotton and dyed in feebly alkaline salt baths. Cotton black 3 G yields the most greenish shades of black, "3 B" the bluest and bloomiest shades, and "R N" the reddest. They are fairly fast to washing, but less fast to light; their fastness to acids and alkalis is satisfactory. By coupling with diazotised paranitraniline, brown-blacks of good fastness to washing are produced, which may be brightened by an addition of Methylene blue to the coupling bath. Cotton black R N dyed direct and topped with Methylene blue yields a rich full black.

**OXAMINE BLACK A, N, R N (B.A.S.F.).**

*Oxamine Black A.*—Blue-black powder; aqueous solution, blue-black; HCl, red-violet precipitate; NaOH, violet solution; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, red-violet precipitate.

*Application.*—Cotton is usually dyed in a feebly alkaline salt bath, with subsequent diazotising and developing. The colours level well and yield, when dyed direct, navy blues which are fairly fast to washing and also to light, and good to alkalis, but not to acids. By developing with beta-naphthol dark blue shades, and, with diamine, jet-blacks are produced, which are very fast to washing and good to acids and alkalis; the fastness to light is satisfactory, and may be increased by a subsequent treatment with copper sulphate.

**GROUNDING BLACK 4 B FOR COTTON (B.A.S.F.).**

Brown-black powder; aqueous solution, violet-black; HCl, brown-black precipitate; NaOH, red solution; solution in H<sub>2</sub>SO<sub>4</sub>, blue-black; on diluting, brown-black precipitate.

*Application.*—This dyestuff serves principally for grounding cotton in unions, and is applied in a lukewarm salt bath (at about 45° C.), when the cotton is dyed considerably deeper than the wool, the latter then being cross-dyed with acid colours in an acid bath.

**DIANIL BLACK (M.L.B.).**

A great number of brands are in the market—*e.g.*, Dianil black G, R, P G, P R, C R, C B, N are in the market.

*Dianil Black R.*—Black powder; aqueous solution, reddish-black; on diluting, dark violet precipitate; NaOH, soluble precipitate and slightly bluer solution; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, violet precipitate.

*Application.*—Dianil black is dyed on cotton in a neutral or feebly alkaline salt bath, and yields various shades of black which are moderately fast to light, fairly fast to washing, and good to acids or alkalis. By a treatment of the direct colours with diazotised *p* nitraniline (Azophor red P N) according to the coupling method, good deep blacks of very good fastness to washing are produced. The coupling method was recommended for the first time for Dianil black R, diazotised benzidine then being used. Dianil black R and C R may also be diazotised and developed on the fibre for the production of deep blues and blacks. A treatment with bichromate and copper sulphate enhances the fastness to light and washing. Dianil black C R and C B serve well as a bottom to Aniline black. Unions and satins may be dyed by the one-bath methods.

**PATENT DIANIL BLACK (M.L.B.).**

A number of brands, such as F F, F F A, F F C, E F, R W conc., &c., are in the market.

*Patent Dianil Black F F conc.*—Greyish-black powder; aqueous solution, violet-black; HCl, black precipitate; NaOH, bluer solution and dark soluble precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, dark green-blue; on diluting, black precipitate.

*Application.*—Cotton is dyed, in a feebly alkaline salt bath, good shades of blue-black and jet-black, which are fairly fast to washing, good to acids and alkalis, but not very fast to light. Owing to their behaviour in the finishing processes, they are very well suited for linings, and they may also serve as bottoms to Aniline black, as they stand the treatment with copper sulphate and bichromate well, and are improved thereby in fastness.

**DIRECT GREY R and B (Ch. Ind. Basle).**

*Direct Grey R.*—Benzidine <math>\begin{cases} \text{dioxy-naphthoic sulphonic acid.} \\ \text{dioxy-naphthoic sulphonic acid.} \end{cases}</math>

*Direct Grey B* is the corresponding tolidine compound.

Both brands show the following reactions:—Dark grey powder; aqueous

solution, violet to blue; HCl, greyish-blue precipitate; NaOH, dark red-violet precipitate; solution in  $H_2SO_4$ , bluish; on diluting, greyish-blue precipitate.

*Application.*—Direct grey is dyed on cotton in a feebly alkaline salt bath, and yields grey to black-blue shades of moderately good fastness.

#### CARBIDE BLACK (Ch. Ind. Basle).

A number of brands, such as R I, B I, S O, &c., show the following reactions:—Grey or black powder; aqueous solution, violet-black or reddish-black; HCl, dark precipitate; NaOH, dark soluble precipitate and change of the colour of the solution; solution in  $H_2SO_4$ , dark blue or blue-violet; on diluting, dark precipitate.

*Application.*—Cotton is dyed, in a feebly alkaline salt bath, black shades, which are fairly fast to washing, acids, and alkalis, but not to light. By coupling with diazotised nitrobenzidine, good catch shades, fast to washing, are obtained with the brands R I and B I; coupling with diazotised *p* nitraniline yields deep blacks of good fastness to washing. Unions and satins may be dyed by the one-bath methods.

#### DIPHENYL BLUE-BLACK (Geigy).

Benzidine  $\left\{ \begin{array}{l} \text{amidonaphthol disulphonic acid H.} \\ \text{ethylamidonaphthol sulphonic acid } \gamma. \end{array} \right.$

Black powder; aqueous solution, black-violet; HCl, dark precipitate, readily soluble with a red-violet colour; NaOH, redder solution; solution in  $H_2SO_4$ , dark violet-blue; on diluting, violet.

*Application.*—Diphenyl blue-black is dyed on cotton in a feebly alkaline salt bath, and yields bluish-grey to dark blue shades which are fairly fast to washing, moderately fast to light, and good to acids and alkalis.

#### DIPHENYL FAST BLACK (Geigy).

*p* Diaminoditolylamine  $\left\{ \begin{array}{l} \gamma\text{-aminonaphthol sulphonic acid} \\ \text{(combined in alkaline solution).} \\ m\text{ toluylene diamine.} \end{array} \right.$

Black powder; aqueous solution, violet-black; HCl, blue-black, precipitate; NaOH, redder solution and soluble dark precipitate; solution in  $H_2SO_4$ , blue; on diluting, blue-black precipitate.

*Application.*—Cotton is dyed with the addition of salt, a deep blue to black, fairly fast to light and washing, and not sensitive to acids or alkalis. Unions and satins may be dyed by the one-bath methods.

#### ISODIPHENYL BLACK R (Geigy).

*p* Phenylene diamine  $\left\{ \begin{array}{l} \gamma\text{-aminonaphthol sulphonic acid—}m\text{ phenylene} \\ \text{resorcin.} \end{array} \right.$  diamine.

Black powder; aqueous solution, violet-black; HCl, blue-black precipitate; NaOH, redder solution and soluble dark precipitate; solution in  $H_2SO_4$ , blue; on diluting, black precipitate.

*Application.*—Isodiphenyl black is dyed on cotton with the addition of salt and yields a deep reddish-black not fast to light, but fairly fast to washing, and good to acids and alkalis. The fastness to washing is considerably improved by a treatment with 4 per cent. formaldehyde (40 per cent.) at 50° C., this treatment having for the first time been recommended for Isodiphenyl black. Unions and satins may be dyed by the one-bath methods.

#### FORMIC COLOURS (Geigy).

Recently a number of formic colours, such as Formic black, Formic blue, Formic brown, &c., have been placed on the market which, similarly to Isodiphenyl black (see the preceding colour), have the common property of being greatly improved in fastness to washing by a treatment with formaldehyde.

**DIRECT BLACK V (Sandoz).**

Benzidine  $\left\{ \begin{array}{l} \text{aminonaphthol disulphonic acid 2 R—}\alpha\text{-naphthylamine.} \\ \gamma\text{-aminonaphthol sulphonic acid.} \end{array} \right.$

Greyish-black powder; aqueous solution, violet-black; HCl, blue-black precipitate; NaOH, red-violet solution; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, blue-black precipitate.

*Application.*—Cotton is dyed in a neutral or feebly alkaline salt bath, violet-grey to violet-black shades, which are fairly fast to washing, moderately fast to light, and good to acids and alkalies. Diazotising and developing with  $\beta$ -naphthol produces a deep navy blue; with diamine, deep black of good fastness to washing.

**TITAN BLACK D, D G, R G (Holliday).**

Black powder; aqueous solution, violet-black; HCl, blue-black precipitate; NaOH, redder; solution in  $\text{H}_2\text{SO}_4$ , green (D), or dark slate (D G, R G); on diluting, blue-black precipitate.

*Application.*—Cotton is dyed in a feebly alkaline or neutral salt bath grey to black shades, fairly fast to washing, and good to acids and alkalies. Unions are dyed by the one-bath method; sometimes a little acetic acid is added about ten minutes before the end of the dyeing operation. Titan black may also be used in a cold alkaline bath for the covering up of burls.

**DIRECT BLACK R (Holliday)** is similar to Titan black.

**TITAN INGRAIN BLACK 2 B and R (Holliday).**

Blue powder; aqueous solution, blue; HCl, blue precipitate; NaOH, soluble purple precipitate; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, blue precipitate. The "2 B" brand is not precipitated by acids or alkalies.

*Application.*—These colours may be diazotised and developed on cotton with the ordinary developers, and yield good navies and blacks of satisfactory fastness to washing, light, acids, and alkalies.

**DIANOL DIAZO BLACK (Levinstein).**

Black-brown powder; aqueous solution, reddish-black; HCl, brown precipitate; NaOH, soluble blue-black precipitate; solution in  $\text{H}_2\text{SO}_4$ , bluish-green; on diluting, brown precipitate.

*Application.*—Cotton is dyed in a feebly alkaline salt bath grey to blue-black shades, fairly fast to light and washing, and good to acids and alkalies. By diazotising and developing with diamine, jet blacks; and with  $\beta$ -naphthol, dark blues, of very good fastness to light and washing, are produced. Unions and satins are dyed by the single-bath methods.

**UNION BLACK, UNION BLUE, UNION BROWN, &c.,** are denominations for various brands of direct cotton colours, which are especially well adapted for dyeing solid shades on unions in one bath. Some of these brands also contain suitable wool colours for shading the wool in the neutral bath.

## SULPHIDE OR SULPHUR COLOURS.

This group of colours, the first representative of which was Cachou de Laval, described in the first edition of this work, has developed enormously during the last decade and become one of the most important class of colours, especially for the production of fast colours on cotton and other vegetable fibres.

The sulphide colours are produced by melting organic substances with sodium sulphide or polysulphide (mixtures of sodium sulphide and sulphur). With the exception of Cachou de Laval, the first sulphide colour obtained, the organic substances used in their production are almost exclusively compounds of



the aromatic series containing nitro-, amino-, or imino-groups, such as dinitrophenol, dinitronaphthalene, *p* aminophenol, *p* phenylenediamine, oxydinitrodiphenylamine, dimethyl *p* oxydiphenylamine, indophenols, safraninones, &c. All sulphide or sulphur colours contain in their molecules sulphur as an essential constituent, and all are dyed in a sodium sulphide bath, hence their name. Some of the older products contain enough sodium sulphide to dissolve the dyestuff directly in water; but the more recent brands are furnished to the trade in a purer condition and dissolve only with the addition of sodium sulphide (or reducing agents like sodium hydrosulphite or glucose and soda, *see below*).

Very little is known of the constitution of the sulphide colours. They probably contain two or more groups of  $-S-S-$  in the molecule, which are dissolved by the action of sodium sulphide with the formation of groups of  $SNa$ , whereby the dyestuffs become soluble. Sodium sulphide being a strong reducing agent, many of the sulphide dyestuffs are reduced on dissolving, and the solutions generally resemble in a certain sense those of vat dyes—*e.g.*, that of indigo—the re-oxidation of the dyestuffs in the liquor and in the fibre, however, proceeding less rapidly than is the case with vat dyes.

Other reducing agents, such as sodium hydrosulphite or glucose (grape sugar) and caustic soda, may also be used for dissolving; but these do not act exactly like sodium sulphide and the colours are not fixed exactly alike, their fastness to washing being usually best when dyed from a sulphide bath. Some of the blue dyestuffs are dyed in a sodium sulphide bath with the addition of glucose, the sulphide alone not being sufficient to keep them perfectly in solution.

Owing to the sodium sulphide contained in the dye-liquors, the sulphide dyestuffs must never be dyed in copper vessels, the copper being severely attacked by the sulphide and copper sulphate which is a very active oxygen carrier being formed in the liquor. Hence, very small quantities of copper are detrimental, and no parts of the dye-vessels, such as coils, steam valves, nails, or other fittings should be made of copper, brass, German silver, or other alloys containing copper. Wood, iron, nickel, lead, hard lead, and rubber do not act detrimentally. It must be noted, however, that the copper is acted upon by the sulphide only, not by the dyestuff; therefore the dyed material, after washing, may come in contact with the metal and may be after treated in copper vessels, or be hydroextracted in a copper cage.

The sulphide colours gradually oxidise under the combined action of air and moisture, and, therefore, they should always be kept in well-closed vessels in a dry and not very hot place.

The sulphide colours are chiefly employed for dyeing fast shades on cotton and linen, and may be used in the same way on all other vegetable fibres, as also on artificial silk. They are of minor importance for wool, although they may be dyed very well by some special methods on this fibre. Neither are they dyed to a great extent on silk, but can be used with advantage for the production of colours very fast to light, washing, boiling-off, and acids. They are also used for unions and satins, the vegetable fibre, however, of these materials being principally dyed by them, whereas the animal fibre is generally dyed in a separate bath by acid or chrome colours.

Basic colours are fixed exceedingly well by sulphide colours, and may serve for topping them.

The sulphide colours are generally distinguished by excellent fastness to light, washing, milling, alkalis, acids, acid cross-dyeing and stoving; with a few exceptions they are not very fast to chlorine.

The sulphide colours are generally brought into the market in the form of powders and some as pastes insoluble in water. Some of the older brands

are sold in the form of lumps containing sodium sulphide, and are, therefore, soluble in water; these, however, rapidly deteriorating in the air, have nearly disappeared. A few of the pure products are slightly soluble in water, but dissolve much more readily on the addition of sodium sulphide. All the sulphide colours readily dissolve in water containing a quantity of sodium sulphide about equal to their own weight; the solubility, however, varies according to the properties of the single dyestuffs and their purity, the impure products of imperfect manufacture requiring the greatest quantities. The solutions are mostly strongly coloured unless light coloured reduction products (leuco-compounds?) are formed. The sulphide solution gradually oxidises in the air whereby the dyestuff is precipitated; an addition of fresh sodium sulphide readily redissolves the precipitate on heating. Hydrochloric acid also precipitates the dyestuff from this solution with the evolution of sulphuretted hydrogen. By hydrochloric acid alone the sulphide dyestuffs are not dissolved, but are gradually decomposed. Neither does caustic soda dissolve them; but as most of the commercial products contain small quantities of free sulphur, they partially dissolve when heated with caustic lye, more or less sodium sulphide being formed. The dyestuffs are gradually dissolved by concentrated sulphuric acid, but much more slowly than most other organic colouring matters, and the solutions in sulphuric acid do not show very characteristic colours; by diluting with water the solutions are precipitated.

Alkaline reducing agents readily dissolve the colours; on oxidation by the air the original colours are formed again. The sulphide colours form lakes with all metals except the alkali metals, and thus their solutions are precipitated by the salts of the alkaline earths, earth metals, and heavy metals.

As may be seen from the preceding remarks, the sulphide colours show almost the same general reactions, and cannot easily be distinguished from each other by the usual methods. We, therefore, refrain from describing them individually, preferring to give only detailed instructions for the best modes of application of the group as a whole.

The following list contains the names of the sulphide colours at present in the market, and of their makers:—

Name of Colours.	Makers.
<b>Amidazol colours,</b> . . . . .	Holliday.
Auronal „ . . . . .	Weiler ter Meer.
Cross dye „ . . . . .	Holliday.
Eclipse „ . . . . .	Geigy.
Immedial „ . . . . .	Cassella.
Katigene „ . . . . .	Bayer.
Kryogene „ . . . . .	B. A. S. F.
Pyrogene „ . . . . .	Ch. Ind. Basle.
Pyrol „ . . . . .	Leonhardt.
Sulphur „ . . . . .	Berlin.
Sulphurol „ . . . . .	Dahl.
Thiogene „ . . . . .	M. L. B.
Thion „ . . . . .	Kalle.
Thional „ . . . . .	Sandoz.
Thionol „ . . . . .	Levinstein.
Thioxine „ . . . . .	Oehler-Griesheim.

Some special names are:—Anthraquinone black, Fast black B and BS (B.A.S.F.), Autogene black, St. Denis black, Vidal black, Cachou de Laval, Thiocatechine (Poirrier), Cattu Italiano, Italian green, Sulphine brown (Lepetit), Melanogene blue (M.L.B.), Sulphaniline black (Kalle), Thiophenol black (Ch. Ind. Basle), Rexoll black (Rexoll, Ltd., Bradford).

**DISSOLVING THE COLOURS.**—The sulphide colours are placed together with the sodium sulphide required for dyeing (or in some cases only a part of the sulphide) in a wooden vessel, and are then brought into solution by simply pouring hot water over them and stirring.

### DYEING OF COTTON AND LINEN WITH THE SULPHIDE COLOURS.—

Cotton and Linen are dyed with the sulphide colours without previous bleaching. Vessels made of wood or iron (or other materials containing no copper) are employed. For heating, steam coils made of iron or lead are used, and the heating is best effected by closed steam coils. The baths used should be as highly concentrated as possible, since the liquors used are incompletely exhausted. Thus, for loose cotton about fifteen times, and for yarns about eighteen to twenty times, the weight of liquor, calculated on the weight of the cotton, is employed. In order to make use of the colour remaining in the bath, standing baths are kept where possible, and these are freshened up with corresponding amounts of dyestuff and the other ingredients. In addition to colouring matter and sodium sulphide, sodium carbonate and sodium sulphate (Glaubersalt), or common salt, are chiefly used. Soda serves for rendering the colour more easily soluble and for converting the calcium sulphate, usually contained in the water, into insoluble carbonate, which will not precipitate the dyestuffs. Glaubersalt and common salt are added for the purpose of better exhausting the bath; they may be used in considerable quantities, but the specific gravity of the bath should not exceed  $10^{\circ}$  to  $12^{\circ}$  Tw. for blacks, or  $4^{\circ}$  to  $5^{\circ}$  Tw. for colours.

The bath is prepared with about 5 grms. soda ash per litre of water ( $\frac{1}{2}$  lb. per 10 gallons) and boiled up, then the colour solution and, finally, the salt is added. In some cases some other additions are made; 2 per cent. (of the

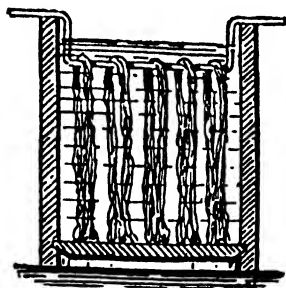
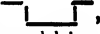


Fig. 57.

weight of the cotton) Turkey-red oil, Monopole soap or Monopole oil—*e.g.*, are used for better levelling; or glucose, for reducing and dissolving; and glue, for enhancing the brightness of certain dyes. The quantities of colouring matter, of course, vary greatly according to the shade desired and the concentration and colouring power of the dyestuff. The quantity of sodium sulphide is usually expressed in proportion to the weight of colouring matter, the average required being the same weight up to double such weight and in some cases even more sulphide. Light shades require a greater proportion of sulphide than deep ones, an excess always being necessary to make up for the sulphide oxidised by the air during the dyeing operation. Too great an excess of sulphide impedes the proper exhaustion of the dye-bath.

Loose cotton is entered without previous wetting into the boiling bath and worked for ten to fifteen minutes. It is then covered with a perforated lid, so as to be submerged in the liquor, and allowed to feed with the steam shut off for one-half to three-quarters of an hour. After this time it is thrown out so as to drain into the dye-bath, or it is hydro-extracted in a machine, the cage of which is made of steel or tinned copper, and well rinsed.

Cotton yarn is best dyed on bent iron tubing (gas pipe), shaped like , which are kept free from iron rust by washing them with soda or by rubbing them with cloth impregnated with mineral oil in the evening. The yarn on these bent pipes is always kept well covered by the liquor, as seen in Fig. 57. Ordinary straight wooden sticks may also be used, although level shades are produced with greater ease on bent sticks. The yarn is usually entered into the boiling bath and given a few turns; then the steam is shut off and the yarn turned about every five minutes. Some colours, principally the bright blues, are dyed in light shades at  $30^{\circ}$  to  $40^{\circ}$  C., and in dark shades at  $50^{\circ}$  to  $70^{\circ}$  C., the colours coming out brighter at the lower temperature. (It should be noted, however, that all sulphide colours can be dyed very well

in a cold bath; it is only necessary to prepare the first bath much stronger with dyestuff and sodium sulphide, the cold liquor being exhausted less.) After working the yarn for three-quarters to one hour, each stick full of yarn is given a few rapid turns, then lifted and squeezed off immediately by a wringing machine worked by hand, and attached to the front end of the vat—for instance, like Fig. 58. This squeezing is very important for the production of level shades—that the adhering liquor be removed, and the dyestuff dissolved be not precipitated on to the cotton when the sodium sulphide is oxidised in the air—the precipitated dyestuff not being removed by rinsing. After squeezing, the yarn in most cases is rinsed without delay. With such colours as come out of the dye-bath in a reduced and soluble state, it is better to expose the well squeezed yarn for some time to the air before rinsing, since much colour would be dissolved and removed if immediately rinsed. Colours which are developed by steaming or smothering must not be rinsed previous to developing (see p. 453).

Piece goods may be dyed in the jigger, or in the padding machine, or in the

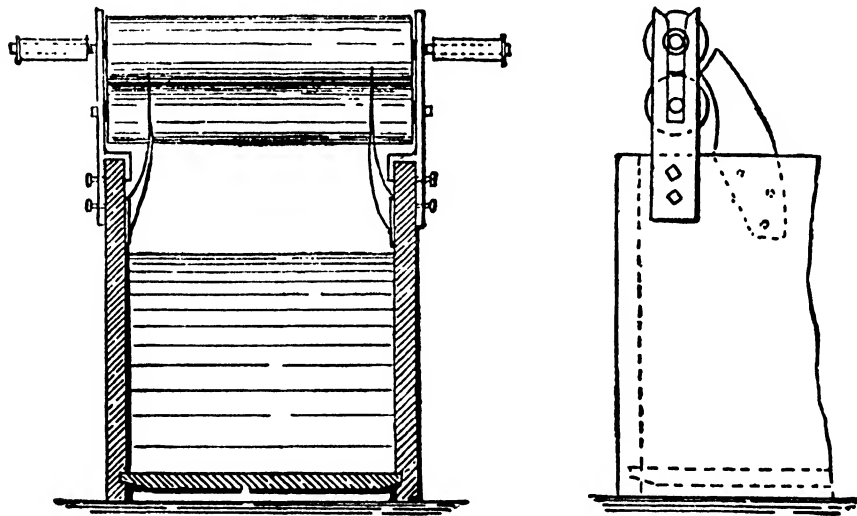


Fig. 58.

continuous machine. Generally the jigger, with squeezing rollers, is used, and for a large output of blacks, blues, and browns the continuous machine. It is very easy to produce level shades in the ordinary jigger, provided pieces of the same width only are dyed in one lot, and are rolled up with the selvages smooth and straight and not protruding over the bulk; it is not necessary to have the pieces submerged in the liquor. The pieces are dyed with six to eight end at the boil—or with the bright blues at a lower temperature (like yarn)—and then squeezed off very evenly, straight rolling up and well squeezing being essential for the production of level shades. After squeezing, the pieces are rinsed immediately in a jigger placed next to the dye-jigger, or, in some cases (see *Yarn*), first passed over a few guiding rollers through the air.

Machine dyeing of loose cotton, sliver, cheeses, and hank yarns has come largely into use with sulphide colours which, owing to their great solubility, are well adapted for this method of dyeing. The hot liquor is circulated for about one hour through the cotton and then removed as completely as possible either

by a vacuum or, less completely, by air pressure; in the latter case, the cotton, after running off the dye-liquor, is sometimes rinsed first with a very weak solution of sodium sulphide. Recently, dyeing machines have been constructed, the dye-vessel of which is a hydro-extractor; this is caused to revolve when the dyeing is finished, so as to remove the dye-liquor without access of air.

Mercerised cotton is dyed like ordinary cotton. It is, however, useful for better levelling, to diminish or, for light shades, to use no salt while increasing the sulphide, and to add some Turkey-red oil. The dyeing is best carried on at a temperature not exceeding 70° to 80° C.

Attention is called to the fact that the careful removal of the adhering liquor from yarns and piece goods on lifting is of supreme importance for the successful production of level shades, and almost all the initial difficulties in the application of sulphide colours are due to neglect in this respect. It is, of course, important that the bath be in a good condition, and the colour be dissolved thoroughly. This is best tested by putting a drop of the liquor on filter paper; if the colour is the same on both sides, the colour is well dissolved; but when a precipitate is observed on the upper side, an addition of sodium sulphide becomes necessary.

The liquor draining from the cotton, yarn, or pieces, which still contains much colour, is usually returned to the bath, and the first wash water is frequently used for replenishing the liquor.

It may be mentioned here that the sulphide colours may be mixed with many of the direct cotton colours for shading, most of the latter resisting the reducing action of the sulphide bath. Since, however, the range of shades obtainable with the sulphide colours is now fairly large the method has gone out of use.

*Topping with basic colours*, on the other hand, is made use of to a great extent for brightening or slightly shading, the basic colours being very well fixed without mordanting. The material dyed with the sulphide colours is simply worked in a cold bath prepared with  $\frac{1}{10}$  to  $\frac{1}{2}$  per cent. basic dyestuff and 2 to 5 per cent. acetic acid (of the weight of the cotton), and after some time the bath is heated to 50° C.

In addition to the dyeing with sodium sulphide various other processes have been proposed—*e.g.*, with sodium sulpho-hydrate ( $\text{NaSH}$ ), sodium thio-carbonate ( $\text{Na}_2\text{CS}_3$ ), sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), or with glucose and caustic soda or carbonate of soda. But none of these processes have acquired any practical importance, the sodium sulphide method being cheap, certain, and working excellently without any detrimental effects (see, for instance, p. 453).

**AFTER-TREATMENT OF COTTON DYED WITH THE SULPHIDE COLOURS.**—Various after-treatments are in use. The *after-treatment with metallic salts*, well known for the substantive dyes, may be employed with advantage for most of the sulphide colours. A mixture of  $1\frac{1}{2}$  to 2 per cent. copper sulphate and  $1\frac{1}{2}$  to 2 per cent. potassium or sodium bichromate with the addition of 3 to 5 per cent. acetic acid (of the weight of the cotton) is especially valuable for enhancing the fastness to light and also to washing of many browns and mode shades generally. It is also used for the same purpose for certain blues or for brightening the latter. This mixture, however, is best avoided for blacks, since copper salts exert a tendering action on cotton dyed with sulphide blacks (*see below*).\* Blacks are best treated with 3 per cent. bichromate and 3 to 5 per cent. acetic acid or with a mixture of 2 to 3 per cent. bichromate,  $1\frac{1}{2}$  to 2 per cent. chrome alum, and 3 to 5 per cent.

\* Copper sulphate must not be applied in iron vessels, the iron being attacked by copper salts.

acetic acid, which treatment also improves the fastness to washing, but chiefly enhances the beauty of the shade; chrome alum makes it more greenish, and bichromate more bluish.

Cotton dyed black with sulphide colours should always be subjected to a final *alkaline treatment* with soda, soap, or other mild alkalis or, if this be not feasible, with 3 to 5 grms. *sodium acetate or formate* per litre water (5 to 8 ozs. per 10 gallons) in order to prevent subsequent tendering of the fibre. Much has been written on the cause of this tendering, but no full and exact explanation has been given. The sulphide used for dissolving, doubtless, has no deleterious effect and, therefore, all the endeavours to replace it by other agents have been useless. Whether the free sulphuric acid, always found in cotton, tendered after being dyed with sulphide colours originates from free sulphur contained in, or by the sulphur chemically combined with the dyestuff has not yet been cleared up. From time to time tendering has occurred, and in most cases with cotton which has been treated with acid, even acetic acid,—*e.g.*, in its after-treatment with metallic salts, or which has been cross-dyed in cotton warp unions. The after-treatment with copper sulphate has been found most harmful, whereas a combination of copper sulphate and bichromate seems to have no special effect. The only method yet known to prevent tendering is to keep the cotton slightly impregnated with a mild alkali or with sodium acetate or formate. These two salts are especially valuable in the case of mercerised and silk-scooped cotton, and of cotton warps to be interwoven with worsted yarns and then to be cross-dyed, since in both cases alkaline salts would not be applicable. Considering the enormous quantities of cotton dyed black with sulphide colours tendering occurs very rarely in spite of the fact that very frequently the alkaline treatment is omitted. This, however, must not be taken as a proof that the treatment is not necessary. It seems that it should be dispensed with in those cases only where alkaline water is used for rinsing, but it is advisable never to neglect this treatment before drying the black cotton and to have it repeated after unions have been acid cross-dyed or otherwise treated in an acid liquor or stoved in a sulphur stove.\*

For *developing* Immedial blue some special methods of after-treatment are in use. The cotton after dyeing is freed by hydro-extracting, pressing, squeezing, or winding from the adhering liquor, and then either placed for about twelve hours in a warm room, care being taken that it will not dry by enveloping it in water-proof cloth or in a cloth saturated with the old dye-liquor, or it is brought into a steam-box and steamed for one-half to one hour with the admission of air. This latter process, which is especially valuable for hank yarns, may be executed in an ordinary yarn vat, steam being blown in through the holes of the steam coil; for blowing in air, a Koerting air injector has to be inserted into the steam pipe; the vat is best covered by a loosely fitting cover made of wooden boards. The time of steaming depends on the quantity of the steam; a good indigo shade should be produced, but the developing must not be pushed too far; although the shade becomes brighter by prolonged steaming the fastness to washing will suffer. With these two methods of developing by smothering or by steaming it is important that the dyed cotton still contains some of the old dye-liquor, and, therefore, the cotton must not be rinsed before developing and must be protected from water drops falling on to it before or during the developing, each drop washing away the old liquor and causing an undeveloped spot. After developing, the cotton is washed hot so as very thoroughly to remove the soluble colour to prevent bleeding; the well-washed cotton will then be

\* This subject has recently been very ably treated by J. E. Pilling (*Journ. Soc. Dyers and Col.*, 1906, p. 55). See also A. Kertess (*loc. cit.*, p. 93).

dyed exceedingly fast to washing. This treatment, however, is useful for certain brands only, most of the sulphide dyestuffs thereby losing in fastness to washing. The treatment with feebly alkaline solutions of hydrogen peroxide yields the brightest shades of blue, but is very little used owing to the expense of the peroxide. The bath is prepared with  $1\frac{1}{2}$  to  $2\frac{1}{2}$  per cent. hydrogen peroxide and as much ammonia, or with  $1\frac{1}{2}$  to  $2\frac{1}{2}$  per cent. sodium peroxide and as much sulphuric acid, and should have a slightly alkaline reaction. The cotton in this case is well rinsed after dyeing and worked in the cold peroxide bath for fifteen minutes, which is then heated within twenty minutes to  $60^{\circ}$  C.; finally the cotton is rinsed and soaped hot. By using greater quantities of peroxide than above indicated the brightness of the blue is increased, but the fastness to washing is deteriorated.

A slight treatment with hydrogen peroxide may sometimes be useful for matching a given shade. Most sulphide colours will oxidise a little more after drying and show a brighter shade after a couple of days. A weak hydrogen peroxide solution completes the oxidation and, if applied to a small sample, will show the final shade of the whole lot. It may be noted, however, that the shades always become slightly brighter and never duller, therefore no inconveniences are caused to the dyer by this change, and the treatment with peroxide is rarely made use of.

*Coupling with diazotised paranitraniline* has been recommended for numerous sulphide browns. This treatment is executed in the way indicated on p. 383, and yields more yellowish and more intense shades of browns.

It may be mentioned that it has also been recommended to dye the sulphide colours on cotton mordanted with metallic salts; but the advantages gained do not pay for the increased expense and labour.

**LINEN AND OTHER VEGETABLE FIBRES** are dyed like cotton with the sulphide colours. Blacks, blues, and cutch shades are dyed to a great extent on linen yarn and linen pieces and also on linen unions.

**DYEING OF WOOL AND SILK WITH THE SULPHIDE COLOURS.**—Wool is dyed very rarely, and silk to a limited extent only, with the sulphide colours. Wool is best dyed with other dyestuffs requiring a neutral or acid bath. But silk is well dyed with these dyestuffs if required to be fast to light, washing, bleeding in water, boiling-off, acids, &c. A process for protecting wool against the action of alkaline liquors and alkaline sulphides by treatment with formaldehyde has been patented by R. Kann.\* The following process † is applicable to both wool and silk and is employed for the production of fast colours on silk. The dyestuff, the necessary quantity of sodium sulphide, and twice as much glucose (grape sugar) as sulphide are boiled together in water for ten minutes. This solution is added to the boiling hot dye-liquor previously prepared, per litre (10 gallons) with 1 gm. ( $1\frac{1}{2}$  oz.) soda ash, 3 c.c. (5 ozs.) Turkey-red oil, and 5 to 10 grms. ( $\frac{1}{2}$  to 1 lb.) Glauber's salt. Silk yarn is dyed in this liquor for one hour, best on bent rods, and then lightly pressed off, rinsed, soaped, and brightened with acetic acid. If the colours are desired to be fast to boiling-off in soap liquor they should be after-treated in a boiling hot bath with 2 per cent. copper sulphate, 2 per cent. bichromate, and 5 per cent. acetic acid, then rinsed and brightened. Black is best dyed on a mordant of nitrate of iron,  $25^{\circ}$  to  $32^{\circ}$  Tw. The glucose is added to the dye solution in order to counteract the deleterious action of sodium sulphide on the animal fibre. Similar effects are produced by tannin: formaldehyde, acids, acid salts, and ammonium salts also serve this purpose to some extent. Organic acids, which possess reducing properties

\* E. P. 3,492, 1903, *Journ. Soc. Dyers and Col.*, 1903, p. 297. See also H. Levinstein, *ibid.*

† E. P. 24,697, 1901, *Cassella, Journ. Soc. Dyers and Col.*, 1903, p. 11.

such as lactic or formic acid, have been made the object of a more recent patent (Farbenfabriken, vorm. Fr. Bayer & Co.).

It is an interesting fact that the addition of glue to the dye-bath in dyeing certain sulphide colours prevents silk from absorbing the dye, thus allowing blacks and colours to be obtained on cotton cloth, preferably mercerised, containing white or dyed silk checking threads, and for the so-called "Grisaille style."\* Wool may be reserved in a similar manner by a previous treatment with formaldehyde and tannin and subsequent dyeing with sulphide colours in a cold or lukewarm bath prepared with glucose (*see above*).† Wool may also be chromed for such two-coloured effects with or without the use of formaldehyde.‡

**UNIONS** may be dyed with the sulphide colours according to the glucose process (p. 454) described above, the cotton being chiefly dyed in this way and the wool being dyed before with colours resisting the alkaline liquor—*e.g.*, acid chrome colours or subsequently with any kind of wool colours. Recently, additions of phosphate, borate, or silicate of soda to the sulphide dye-bath have been recommended in order to protect the wool or silk in unions and satins against the action of the sulphide.

**SATINS** may also be dyed by the glucose process (p. 454). Blacks after chroming are topped with logwood.

**DETECTION OF THE SULPHIDE DYES ON THE FIBRE.**—The following reaction may serve for this purpose:—On boiling with a solution of stannous chloride sulphuretted hydrogen is developed, which is easily detected by the browning of filter paper moistened with a solution of acetate of lead. This test, however, is liable to give misleading results if the fibre contains other sulphur compounds. According to A. G. Green and F. G. C. Stephens,§ the main sources of error appear to be sulphur compounds present in the finishing material, bisulphite compounds of mordant colours and sulphur on the cotton derived from the use of antichlor after bleaching. These sources may be avoided by boiling the sample of cotton for one or two minutes in a 10 per cent. solution of caustic soda before applying the stannous chloride test. When much albumen is, or may be, present (*e.g.*, with calico prints), it is advisable after boiling with caustic soda to boil also with hydrochloric acid. The stannous chloride test after washing out the sample is carried out in the following way:—The sample is just covered with a solution of stannous chloride, obtained by dissolving 100 grms. in 100 c.c. hydrochloric acid and 50 c.c. water. The mouth of the test tube is closed by a cap of filter paper firmly wrapped round it, into the centre of which is placed 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 eventually disappear again on boiling the solution longer, owing to the decomposition of the lead sulphide by the hydrochloric acid evolved. In place of stannous chloride a dilute solution of titanous chloride may be used for this test. The solution should be boiled for about a minute before use as this commercial product frequently contains  $H_2S$ .

Another source of error may be the presence of other substantive cotton colours containing sulpho-groups or sulphur otherwise bound, like Primuline. These are detected by their property of bleeding out on boiling with caustic soda, especially in the presence of white cotton which will be dyed by them:

\* E. P. 14,581, 1902, Cassella, *Journ. Soc. Dyers and Col.*, 1903, p. 232.

† E. P. 25,971, 1906, Cassella, *Journ. Soc. Dyers and Col.*, 1908, p. 174.

‡ E. P. 3,609, 1907, and 13,132, 1907, Bayer, *Journ. Soc. Dyers and Col.*, 1908, p. 147

§ *Journ. Soc. Dyers and Col.*, 1907, p. 118.



these also develop the sulphuretted hydrogen much more slowly than sulphide colours do.

In general the sulphide colours are recognised by their great fastness to soaping without any tendency to bleeding, and by their property of being reduced by hydrosulphite solution, the colour returning under the influence of the air.

Sulphide blacks are distinguished from Aniline black by their inferior fastness to chlorine on a comparative treatment of samples of the two in a test tube. If sulphuric acid is poured over samples of a Sulphide black and of Aniline black, and after a few minutes water is added, the liquid of the Sulphide black acquires a violet hue, and that of Aniline black becomes more greenish.

The stannous chloride test, of course, is not applicable to wool, but the great resistance of sulphide colours to washing, their behaviour towards reducing agents, and the absence of metallic mordants will indicate their presence fairly well.

### BASIC COLOURS.

The basic colours are the salts of organic bases of artificial origin. Their colour-bearing or chromophorous group is contained in the base, hence the name, "basic colours." In the dyeing of the various textile fibres the dyestuff salts present in the dye-bath are decomposed; the acid remains in solution, while the colour base combines with an acid already present in or on the fibre, and thus gives rise by chemical action to a real coloured insoluble, or sparingly soluble, salt or lake, which forms the dye. In the case of the vegetable fibres, cotton and linen, this acid must usually be deposited in the fibre by mordanting with tannic acid, Turkey-red oil, &c., whereas the animal fibres act by themselves as acids: hence they are dyed without mordants. Jute behaves like tanned cotton.

All the basic colours possess the property of dyeing cotton mordanted with tannin or other acid-mordants—*e.g.*, Turkey-red oil or soap—and the same dyestuff always assumes on the different mordants a more or less similar shade. Even the shade is not materially altered if any of the acid-mordants is fixed by different metals, either antimony, or tin, or aluminium, &c. Hence these dyestuffs are *monogenetic*.

The basic colours vary greatly in their general physical and chemical properties, in their constitution and their chromophors, and, lastly, in the brilliancy and fastness of their shades. A large number, like Magenta, Malachite green, Rosaniline blue, and Methyl violet are derivatives of *triphenyl-*

*methane*, and are characterised by the chromophorous group  $\begin{array}{c} \text{R} \\ \diagdown \text{C} \\ \diagup \text{R} \\ \text{R}=\text{N}=\end{array}$ .

They are distinguished from most of the other basic colouring matters by superior beauty, but associated with great fugitiveness. Many of the basic colours, like the Safranines, New blues, and Indulines, are azine-derivatives,

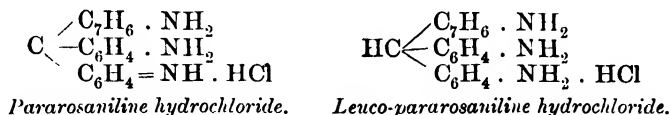
containing the colour-bearing group  $\begin{array}{c} \text{N} \\ \diagdown \text{C}_6 \\ \diagup \text{C}_6 \end{array}$ ; still others, like Phosphine

and Acridine-orange, owe their tinctorial properties to the phenyl-acridine

radical  $\begin{array}{c} \text{C} \\ \diagdown \text{C}_6 \\ \diagup \text{N} \\ \diagdown \text{C}_6\text{H}_5 \end{array}$ ; Methylene blue and allied colours, as also Thioflavine,

contain sulphur as an essential constituent; and, lastly, some, like Chrysoïdine and Bismarck brown, are azo-colours.

All the basic colours are decolourised by reducing agents, like zinc and hydrochloric acid. In the case of the azo-colours a disruption of the molecule takes place, Chrysoïdine being converted into Aniline and triamidobenzene, whilst Bismarck brown yields metaphenylene diamine and triamidobenzene. Almost all the other basic colours are converted by the action of nascent hydrogen into colourless so-called *leuco-compounds* (*i.e.*, white compounds, from the Greek word *leukos*, for "white") which contain two atoms of hydrogen more than the original substances, and are, in most cases, readily reconverted into the dyestuffs by oxidising agents, often simply by the action of atmospheric oxygen.



The Safranine azo-colours, like Indoine or Naphtindone, are split up by reduction, and cannot be regenerated by oxidation; one product of the reduction is, however, the leuco-compound of Safranine, which forms Safranine under the influence of the air; hence, after some time, the solution of the reduced colour becomes pink-coloured, whereby these dyestuffs may be easily recognised.

The basic colours are brought into commerce generally as salts of hydrochloric acid; some as acetates, oxalates, sulphates, nitrates, or as double salts of hydrochloric acid and zinc chloride; in rare cases, in the form of the colour base in the free state. They are sold as powders, crystals, or in rare instances as pastes. Most of the basic colours are soluble in water, while all dissolve in alcohol. On addition of the hydroxides or carbonates of the alkalis and alkaline earths to the solutions, in most cases, the colour bases are thrown down in the free state, most of them being sparingly soluble or insoluble in water, but soluble in alcohol or ether.

If the water used in dyeing contains considerable quantities of carbonate of calcium or magnesium (*i.e.*, if it shows great temporary hardness) it may act on the colour by throwing down the colour base in the form of a curdy precipitate, and thereby rendering a part of it useless for dyeing purposes; while further injury may be done by the precipitate being deposited on the goods, thereby giving rise to spots and unevenness. If the alkalinity of the water is neutralised by the addition of acid this does not take place.

The following experiment is very instructive:—If equal weights of wool are dyed with equal quantities of dyestuff dissolved in one case in distilled water, and in the other in calcareous water, the material acquires a greater depth of colour in the former bath than in the latter. If each bath has been entirely decolourised by the wool, the first remains colourless on the addition of acid, being thoroughly exhausted; whereas in the second bath the colour distinctly reappears; in this latter case that part of the dyestuff which has been precipitated in the form of the colourless base becomes visible by being converted into the coloured salt, and passing into solution. Hence it is often advisable, especially in the case of wool and silk, to dye in a slightly acidulated bath; an excess of acid, however, prevents the bath from being exhausted.

It has already been stated that the wool fibre acts as an acid towards the basic colours, and in the light of this fact we can understand the behaviour of wool and dyestuffs towards each other. In an alkaline bath—*i.e.*, in one containing much calcium carbonate—the wool fibre readily takes up all the colouring matter which is present in solution, both free and combined; but that part which is not dissolved is only gradually attracted. In neutral, or slightly acid, baths, the acidity of the wool fibre is strong enough to decompose

the colour salt and to combine with the bases. A large amount of acid in the free state, however, prevents, more or less, the formation of the compound between the fibre and the base; hence strongly acid baths are not exhausted.

The basic colours are distinguished by great tinctorial power and, generally, by their purity and brilliancy of shade which, amongst dyestuffs, can only be matched by those of the Eosins, and very few of the other artificial colouring matters. These great advantages are largely counterbalanced by their fugitiveness to light and their limited fastness to soaping and milling. Some, like Methylene blue and the Indulines, it is true, are considerably faster than the rest. The fastness to light and air on the various fibres varies in a very irregular way, Magenta being faster on wool than on cotton, whereas Safranin and Methylene blue show the inverse behaviour. An attempt has been made to impart to the basic colours greater fastness to light by treating the dyed goods with a solution of copper sulphate, which process gives excellent results with other dyestuffs (*e.g.*, Benzoazurin); but the great alteration of shade precludes this process being generally adopted.

A number of basic colours are transformed by the action of strong sulphuric acid into sulphonic acids and are thereby converted into acid dyestuffs. The shades of the latter are similar to those of the mother substances, but in their other dyeing properties they are thoroughly changed.

By the following method it can be determined whether a dyestuff belongs to the basic colours or not:—

Dissolve 100 grms. (3 ozs.) each of tannic acid and of sodium acetate in 1 litre (1 quart), add a few drops of this solution to the clear solution of the dyestuff in question, and heat gently; the reagent forms a precipitate with basic colours, whereas the solutions of other dyestuffs, except those of sulphide colours, remain clear; the latter, however, if soluble at all in water, will be easily distinguished by developing the smell of sulphuretted hydrogen on adding a few drops of hydrochloric acid. To detect basic colours on the fibres, the material may be treated with caustic soda (so as to separate the colour-base in the free state), subsequently washed with water, and dried; the colour-base is then extracted with ether, the latter evaporated, and the colour-base finally dissolved in water containing an excess of acetic acid to form the acetate. The solution can then be examined as indicated, or tanned cotton may be dyed in it after evaporating off excess acid. For a rough examination as to whether a basic dye is present, it will be sufficient to treat the dyed material in a test tube with caustic soda, cool off, add some ether, and decant this carefully into another tube; if on adding some dilute acetic acid to the ethereal solution, the former becomes coloured, one or several basic dyes are present. In a similar way the colouring matter itself may also be examined.

The basic colours were the first artificial or so-called aniline colours introduced on a large scale into commerce. They have rapidly won the favour of the public by the great beauty of their shades, and they are used even to-day in large quantities, in spite of the many other dyestuffs invented during the last fifty years, many of which are either faster to light or less expensive. They are, to a very great extent, replaced by the direct cotton colours and the sulphide colours in the dyeing of cotton goods, but they are used still in large quantities in calico-printing. In wool-dyeing they have been almost superseded by the various colours which are dyed in acid baths, while they are still of great importance to the silk-dyer whose customers desire fine tints without regard to fastness. Jute is also much dyed with the basic colours.

**METHODS OF DYEING WITH THE BASIC COLOURS.**—The basic colours are dyed in neutral or slightly acid or sometimes in alkaline baths. Hard water is corrected by the addition of acid; in the case of cotton and silk, acetic acid is generally used; for wool, acetic, hydrochloric or sulphuric acid, bisul-

phate of soda, and alum are employed. A great excess of acid in the dye-bath must, however, be avoided, as it prevents its complete exhaustion.

On account of the great tinctorial power of many basic dyestuffs, small quantities are sufficient to produce full shades. Magenta and others give full shades with 1 per cent., and medium shades with  $\frac{1}{3}$  to  $\frac{1}{2}$  per cent. of dyestuff. For very dark shades 3 per cent. of dyestuff and even more are sometimes necessary.

The basic colouring matters are almost completely taken up from the dye-bath unless a large amount of dyestuff be used or the bath be too acid or alkaline. All the basic colours can be mixed and dyed together in one bath to produce compound shades; but they will not always be attracted by the fibres equally well.

*Dissolving the Colours.*—The basic colours must be dissolved with special care. It is best to use condensed water, or water which has been slightly acidulated with acetic acid. The most suitable temperature is 80°, since some dyestuffs (e.g., Auramine, Nile blue and Methyl green) do not stand a boiling heat. The best method of dissolving is to pour hot water over the colour, and then to stir well, or to dissolve the colour with water in a steam-jacketed pan with frequent stirring (not directly over a fire). If the solution has been standing for some time, and any of the colour has crystallised out on cooling (Magenta, Crystal violet and Auramine being most liable to do this), the dyestuff is redissolved by warming and stirring; it is better, however, to avoid this by dissolving as much colour as is required for immediate use only.

Colours which are insoluble in water are dissolved in dilute alcohol in a closed pressure boiler on a water-bath or steam-bath. In an open vessel loss of alcohol from evaporation would result. About 50 parts of methylated spirits and 50 parts of water are required for 10 parts of colour.

For printing purposes the solutions are often prepared in different ways.

The colours are filtered through cotton, flannel, or a hair-sieve before being used, in order that no undissolved parts may pass into the dye-bath and soil the goods.

**DYEING OF COTTON WITH THE BASIC COLOURS.**—Before dyeing, the cotton is well boiled in soda ash, and, for light and brilliant shades, it has also to be bleached; for dark indigo, brown and black shades, bleaching is not requisite. Some of the basic colours (e.g., Safranine, Methylene blue, and Bismarck brown) dye light shades on unmordanted cotton; this is taken advantage of for producing delicate tints on bleached cotton; but the shades thus obtained are not fast. Indoine, Naphtindone, Janus blue and similar colours can be dyed very well on unmordanted cotton. A very few colours of the induline class (e.g., Toluylene blue and Malta grey) yield full and fast colours on unmordanted cotton by a treatment in bichromate of potassium after dyeing. Generally the cotton must be prepared, however, with mordants before being dyed with the basic colours.

The methods of mordanting may be classed as follows:—

- (1) Mordanting with tannins;
- (2) Mordanting with Turkey-red oil or soap;
- (3) Previous dyeing with other dyestuffs which serve as mordants.

The sulphides of zinc and tin are capable of acting as mordants for the basic colours. The zinc salts of hydroferrocyanic and hydroferricyanic acids (i.e., the precipitates of zinc salts with yellow and red prussiate of potash) have also been proposed as mordants.\*

(1) *Tannin-mordants.*—The tannins form lakes with the basic colours, which are insoluble in water, but dissolve in excess of tannic acid. Hence the colours are not fixed well and are not fast to washing on the tannins alone.

\* Balanche, *Journ. Soc. Chem. Ind.*, 1882, p. 182; C. Reber, *ibid.*, 1885, p. 343.

The tannin, however, can be converted, as previously explained (p. 189), by various metals into insoluble compounds, which also have the power of forming lakes with the basic colours, but do not dissolve them.

The metals used for this purpose are antimony, zinc, tin, iron, titanium, and aluminium; chromium has also been proposed, but offers no advantage. None of the other metals can compare in importance as fixing agents with antimony, which imparts the greatest fastness to light and to soap. Zinc is also very effective. Tin is inferior as to fastness; but the colours are taken up less rapidly and dye more evenly; it is also cheaper. Iron produces dark and dull shades; and aluminium is used only in special cases. Titanium has also been proposed and yields fast colours; it is, however, applicable for certain shades only owing to the intense yellow colouration it imparts to the cotton.

The solutions of the tannin-lakes of the basic colouring matters are, as a rule, duller than the solutions of the pure colour salts. This explains how it is that when dyed on tanned cotton they are not so bright as on wool or silk or on oil-mordanted cotton.

The modes of mordanting and fixing are referred to in the chapters describing the materials employed. For light and medium shades 2 to 5 per cent. of tannic acid (of the weight of the cotton) is required when the mordanting is done by the steeping method; for dark shades the amount required rises to 10 per cent. For the latter, sumach or gallnuts, &c., can be employed with advantage (5 to 10 times as much as tannic acid would be necessary, according to quality); but pure light shades cannot be obtained with ordinary tannin materials, on account of the reddish colouring matters they contain. With the best qualities of *decolourised* sumach extracts delicate tints can be produced. On pieces which are mordanted by slop padding, the amount of tannin varies, according to the shade required, from 2° to 3° Tw. (see p. 189).

*Note.*—In the following the term “tannin” will be used to denote all kinds of tannin-mordants, leaving it to the judgment of the dyer whether he shall select tannic acid, sumach, decolourised extracts, or any other. The quantities refer to tannic acid (gallotannic acid) unless otherwise stated.

The cotton is steeped in the solution of tannin-mordant at a temperature not much higher than 60°, and left in the bath for some hours or overnight; it is then slightly rinsed in cold water, and either dyed directly or passed into the fixing bath.

The tannin-bath can, with fresh additions of tannin, be used continuously until it becomes too dirty. (See p. 189.)

For fixing with antimony the various antimony salts described can be employed. About  $\frac{1}{2}$  to 3 per cent. of tartar emetic (or corresponding quantities of other antimony salts) and the indicated amounts of soda are used; the bath is kept of such a strength as to contain about 10 to 20 grms. of tartar emetic per litre (1 to 2 lbs. per 10 galls.), and is used at a temperature of about 30° to 50°. The baths are also used continuously and their strength is restored from time to time, while the acid produced in the fixing process is carefully neutralised.

The cotton must be washed very carefully after having been treated with antimony, since superficially fixed antimony will not only give rise to rubbing of the ultimate colour, but is liable to affect the skin. For the dyeing with some colours (*e.g.*, Methylene blue and Victoria blue) the washing with water alone is not sufficient to obtain even shades. The cotton is in this case worked for 20 to 30 minutes in a warm soap-bath containing per litre (10 galls.)  $1\frac{1}{2}$  grms. ( $2\frac{1}{2}$  oz.) of neutral soap. It is finally made ready for dyeing by a thorough washing in water. This soaping is generally of advantage for the production of clear and even shades. The risk of rubbing is lessened, and

the fastness to washing, milling, and acid cross-dyeing increased by passing the dyed goods anew through a tannin-bath; the excess of antimony is fixed by this after-treatment. The goods must be rinsed again in water when thus tanned after dyeing, as an excess of tannin would soil the shade. Frequently both the old tannin-bath and the old antimony-bath are strengthened with half the quantity of mordant used for the first bath, and the cotton is then passed through and finally washed; this will give still greater fastness, especially to acid cross-dyeing. This second treatment with tannin, &c., is also of good service, if metals other than antimony are used as fixing agents.

For the fixation with tin, stannic chloride (see p. 277), or in certain cases stannous chloride, is used.

Iron is employed in the form of various salts (copperas, pyrolignite of iron, nitrate of iron). It is of advantage to pass the goods after the treatment with iron through very weak lime water. Sometimes the cotton is treated with iron salts, after having been mordanted with tannin and antimony, to obtain greater fastness to washing, or it is "saddened," after dyeing, in basic nitrate of iron (see pp. 267, 268).

Aluminium is used in the form of basic alum or aluminium acetate; in either case of 1° to 2° Tw. (see p. 234).

The fixation with zinc has not found favour with dyers. It has been recommended to use a bath containing about 10 grms. (1 lb.) of zinc sulphate and 5 grms. ( $\frac{1}{2}$  lb.) of sodium acetate per litre (10 galls.) More recently zinc lactate has been recommended for the same purpose.

When cotton pieces are worked in a jigger or in a padding machine the processes of tanning and fixing are generally the same; but much stronger liquors are used in order to shorten the time required to incorporate the materials with the fibre.

(2) *Turkey-red Oil and Soap as Mordants*.—These two materials, like tannic acid, are fixed on the cotton, before dyeing, in the form of more or less insoluble metallic salts. They yield shades which are brighter than those produced with tannic acid, but are not at all fast to soaping, while they are very fugitive to light. The mode of operation is as follows:—For 10 kgs. (10 lbs.) of cotton prepare a bath with 20 litres (2 galls.) of water and 2 kgs. (2 lbs.) of Turkey-red oil or neutral soap. Soak the cotton in small portions in this bath three or four times for two to three minutes, wring out, and dry at a moderate heat, as described in detail with the Eosins. Subsequently, work the cotton at about 50° for half an hour in a bath containing in 100 litres (100 galls.) about  $\frac{1}{2}$  litre ( $\frac{1}{2}$  gall.) of aluminium acetate (8° Tw.), wash, wring out, and work once more in a weak soap bath, 1 gr. (1 lb.) of neutral soap in 1 litre (100 galls.) of water; finally, wash thoroughly and dye.

(3) *Colouring Matters as Mordants*.—The basic colours can be used with good results in topping almost any other colours. As we have seen in the preceding chapters, both the direct cotton colours and the sulphide colours are topped with the basic dyestuffs, and thus both may become fast to washing. Numberless compound shades can be produced in this way. The basic colours are also used to brighten the shades obtained with Alizarins, logwood, and Aniline black, by topping. Mention may also be made here of the dyeing, first, with Catechu, and, subsequently, with basic colours, although Catechu may be considered as a tannin-mordant. In these cases the first dyestuff, or the dyestuff together with the mordants by which it has been fixed, act as acids towards the colour-base, and bind it on the fibre.

*Process of Dyeing Proper*.—In whatever manner the cotton may have been prepared, it is always dyed by the following method:—A separate bath is used to which the colour is added, during the dyeing, in small portions, in order to effect level dyeing. If the colour is apt to dye unevenly, an addition

of some acetic acid will cause it to go more slowly and evenly on to the fibre. The cotton is entered into the dye-bath at, or a little above, the ordinary temperature, and the dyeing may be finished, without heating, in from thirty to sixty minutes. By raising the temperature to 50° to 60° C. the colour is fixed somewhat better, but further heating is of no use, as a rule, and often the shade loses thereby in brilliancy. After dyeing, the material is wrung, or hydro-extracted, and dried. Rinsing in water after dyeing may be dispensed with; it is certainly not advisable, unless the goods were mordanted with tannin and subsequently with a metallic salt. As has been explained on p. 461 a treatment of the dyed goods with tannin makes the colour still faster to soaping and rubbing.

The basic azo-compounds of Safranine (Indoïne, Naphtindonc, Diazine blue, Janus blue, &c.) and certain basic polyazo-compounds, known as Janus colours, can be dyed fairly well on unmordanted cotton, and when so dyed may be fixed by subsequent mordanting.

The dye-bath should be made slightly acid by the addition of 1½ to 2 litres (galls.) acetic acid or about 600 grms. (9½ ozs.) sulphuric, hydrochloric, or oxalic acid per 1,000 litres (galls.); in the case of soft water 2 to 4 per cent. chromium fluoride or chrome alum may be added for light shades and 3 to 5 per cent. zinc sulphate for dark shades in order to produce more level and fuller colours. After the colour solution is added the dyeing may be commenced between 60° to 100°; after one-quarter to one-half hour's working 10 to 25 per cent. common salt is added in order to better exhaust the bath, some colour always remaining in the bath, especially so in the case of dark shades. The colours thus obtained are fairly fast to washing and fast to acids, but not as a rule very fast in other respects.

In order to improve the fastness the dyed material, after a light rinsing, may be treated in a second bath with tannin and antimony kept in solution by the addition of 1½ to 2 kg. (lbs.) sulphuric acid or oxalic acid per 1,000 litres (1,000 galls.). The hotter the bath the faster the colour will be, but also the duller. Finally the cotton is rinsed and soaped.

Dyeing and mordanting with these colours may also be done in a single bath by adding, together with the common salt (see above), as much salt of antimony as colour used, then boiling three-quarters of an hour and adding twice as much tannin as colour used; a further heating to 60° to 100° for one-quarter to one-half hour will completely fix the colour.

The single-bath process is largely used for light shades. The dye-bath is prepared with 3 to 6 per cent. acetic acid (50 per cent.), ¼ to 1 per cent. basic colour, and 2 to 4 per cent. tannic acid. Dye first cold, then raise to 50° C., and turn ten to fifteen minutes. To increase fastness treat subsequently with tartar emetic. Light shades easily got level in this way.

The basic colours, with a few exceptions, are not at all fast to light and not very fast to soap. Their shades, when produced on tannin in combination with metallic salts, lose by soaping more in depth than the direct cotton colours; but they are not liable to tinge the white fibres in contact with them; hence they are more suitable for calico-printing than the latter.

When dyed on tannin-mordants which have not been fixed with metallic salts and on the other mordants the basic colours are not at all fast either to soap or to light.

**LINEN** is mordanted and dyed with the basic colours exactly like cotton.

**JUTE** does not require any mordants. It is dyed without any additions in boiling baths, or at as high a temperature as permissible, washed, and dried.

**DYEING OF WOOL WITH THE BASIC COLOURS.**—Wool has a great affinity for the basic colours. It attracts them readily from their neutral solutions; hence it is easily dyed with them in a neutral bath. In very hard

water, however, the colour base is precipitated in a sparingly soluble form, as explained above (p. 457), and is not taken up by the wool fibre so readily as in the form of a salt. Wherever possible, the bath is slightly acidified with acetic, hydrochloric, or sulphuric acid, sodium bisulphate, or alum. An excess is avoided, since it prevents the complete exhaustion of the bath.

In dyeing with Methyl green and the Benzaldehyde greens, the bath is not exhausted so well by ordinary wool as by wool which has been mordanted with thiosulphate of soda (*cf.* p. 476).

Wool is dyed with the basic dyestuffs according to two methods.

*First Method.*—The dye-bath is made slightly acid and the colour solution added; the well wetted wool is entered at a moderate temperature, which is gradually raised to boiling. After fifteen to thirty minutes working at the boil, the temperature is allowed to fall to from 60° to 70°, the wool is taken out, washed without much delay, and dried. Brighter shades are obtained by cooling the wool still further in the dye-bath; a part of the liquor is run off and cold water is added, until the temperature has been lowered to 40°; a small amount of neutral soap is then added to the bath and the wool turned for ten minutes, washed, and dried.

*Second Method.*—The dye-bath is not acidulated, and 2 to 4 per cent. of soap may be added to make the shade brighter; but, then, the bath is not exhausted, and should be kept for further use. The dyeing proceeds as by the first method.

The addition of soap to a dye-bath prepared with double salts of zinc (in which form certain colours are sold) is injurious, as it causes the formation of a sticky zinc soap.

Certain colours (*e.g.*, the Benzaldehyde greens and Victoria blues) must be dyed in strongly acid baths.

A number of basic colouring matters are dyed by different methods, which will be described in the special part of this chapter. Special attention may be called to the production of exceedingly brilliant shades with Auramine, Victoria blue, and a few other dyes, by stoving the dyed yarn (stoved or sulphurised colours).

Most of the basic colours are not quite so fugitive to light on wool as on cotton. In fastness to milling they vary exceedingly; some (*e.g.*, Victoria blue, Night blue) are very fast, while others are stripped from the fibre and tinge the white in contact with them. They are not fast to acids (carbonising) or chlorine, and only a few of them withstand stoving.

**DYEING OF SILK WITH BASIC COLOURS.**—Silk attracts the basic colours even more readily than wool, and evinces a stronger acid character towards the colour bases than the latter; thus Methyl green and the Benzaldehyde greens are more easily taken up by the unmordanted silk fibre than by wool.

Silk is dyed with the basic colours in a neutral or alkaline bath or in one slightly acidulated with acetic, tartaric, or sulphuric acid. Water alone or soap solution or "boiled-off liquor" is used in dyeing. 1½ to 2 per cent. of neutral soap (of the weight of the silk) or 10 per cent. of boiled-off liquor (of the volume of the dye-bath) are used. When silk is dyed in acidulated water—*i.e.*, without the addition of soap or other substances—about 3 grms. (1½ ozs.) of acetic or tartaric acid are used for every 10 litres (10 galls.) of (pure) water; and when it is necessary to dye in acidified boiled-off liquor, sufficient sulphuric acid is added to impart a distinctly sour taste and an acid reaction. The colour solution is added, gradually or at once, to the dye-bath; the silk is entered at a moderate temperature and turned frequently, while the liquor is slowly heated to 60° or 80° or sometimes to the boil. After dyeing, the silk is thoroughly washed in water and then usually passed through a very weak



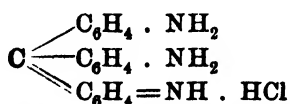
acid bath for *brightening*. Colours which have been brightened with inorganic acids are liable to change on exposure to the atmosphere; it is best to use solutions of about  $1\frac{1}{2}$  grms. ( $\frac{1}{4}$  oz.) of acetic or tartaric acid per 10 litres (10 galls.) of water. After the brightening the silk is wrung out or hydro-extracted and dried. The fastness of the basic colours on silk is about the same as on wool. Most of them are not fast to light nor to washing or water; Aniline blue, Victoria blue, and Night blue are notable exceptions respecting fastness to washing. By a treatment with tannin or antimony and antimony after dyeing the fastness to washing is greatly improved.

**DYEING OF MIXED GOODS WITH THE BASIC COLOURS.**—Union goods (*cotton and woollen mixed goods*) can be dyed with the basic colours. The cotton fibre is first mordanted, as described for cotton goods, with tannin and antimony, &c.; but the temperature of the tannin-bath must not exceed  $45^\circ$ ; if it does, the wool fibre takes up some tannin and subsequently too much colour. The dyeing is effected in a neutral or slightly acid bath; the goods are entered at about  $40^\circ$  and the temperature is gradually raised to the boil. Since it is better to dye wool with acid colours, dyers generally prefer to treat union goods first in a bath with acid colours so as to dye the wool fibre (*sour dyeing*), wash, mordant below  $45^\circ$ , and then to dye the cotton cold in a fresh bath with basic colours until the shade is uniform. Although wool evinces little affinity for the basic colours in cold solutions it is dyed by them to some extent; hence the full depth of shade desired should not be given to the wool fibre with the acid colours, since it is somewhat deepened in the second dye-bath.

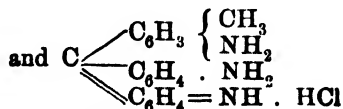
The above (p. 462) mentioned basic colours, the so-called Janus colours, can be used for dyeing unions in one bath. The dye-bath is prepared with 1 to 4 per cent. sulphuric acid and the dyestuff; enter the goods at  $60^\circ$  and heat to  $75^\circ$  or to the boil; if, after three-quarters of an hour, the wool is still too light in colour, heat to the boil and add 5 to 15 per cent. Glaubersalt; but if the cotton is still too light, allow to feed without further heating in a similar way as in dyeing with direct cotton colours. Basic colours dyed in this way possess a fair amount of fastness, but show, like almost all basic colours on wool, a want of fastness to rubbing.

**Half Silk Goods (*Satin*).**—Many colours do not dye well on silk which has been impregnated with tannin. For this reason half-silk goods are first dyed with basic colours by the methods given for silk dyeing so as to dye the silk fibre; and, subsequently, they are mordanted with tannin, &c., and cotton-dyed at as low a temperature as possible. The same precaution has to be observed, as in the case of "sour-dyeing" of union goods, not to dye the silk a deeper shade than desired. Another method of dyeing satin goods with basic colours is carried out in the following manner:—The material, consisting of raw silk warp and cotton weft, is first mordanted with tannin and stannic chloride ( $24^\circ$  Tw.), then boiled off in the usual way with soap, and both fibres dyed in one bath. The silk is thus weighted. Janus colours may be dyed on satin goods in a bath containing 10 to 20 per cent. acetic acid and 2 to 5 per cent. tannic acid; enter cold and heat only to  $35^\circ$  to  $40^\circ$  after the cotton has nearly attained the desired shade.

**MAGENTA or FUCHSINE.**— $C_{19}H_{18}N_3Cl$  and  $C_{20}H_{20}N_3Cl$  :—



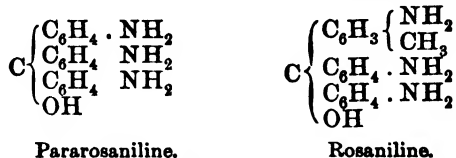
Pararosaniline hydrochloride.



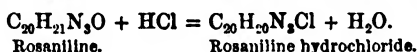
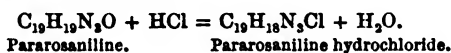
Rosaniline hydrochloride.

Magenta was brought into commerce as early as the year 1859, when it surprised and delighted the world by its brightness, purity, and richness of colour. It has been offered to the trade under a great many other names, as *Aniline red*, *Rubine*, *Roseine*, *Azaleine*, *Solferino*, &c., but at the present time it is generally sold under the names of *Magenta* or *Fuchsine* only.

Various brands are met with in commerce, the purest of which are those of blue shade (extra, double refined, diamond crystals); even these are not chemically uniform substances, but mixtures of the salts of two homologous bases; pararosaniline and rosaniline, which are derivatives of triphenylmethane and tolyldiphenylmethane respectively. Pararosaniline is triamidotriphenylcarbinol and rosaniline is triamidotolyldiphenylcarbinol.



Pararosaniline and rosaniline form Magenta by combining with hydrochloric acid, as shown by the following equations:—



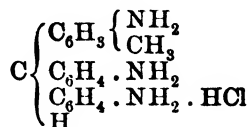
The properties of pararosaniline and rosaniline differ little; rosaniline is present in greater quantities in the commercial product than pararosaniline, and for simplicity's sake we shall mention in the following only rosaniline; but by this name we imply mixtures of rosaniline and pararosaniline.

*Rosaniline base*—i.e., rosaniline in the free state—is precipitated from the hot concentrated solutions of rosaniline salts on addition of caustic alkalis or alkaline earths. It forms almost colourless leaflets, which are very sparingly soluble in water, but dissolve freely in alcohol.

Rosaniline is destroyed by strong oxidising agents, such as chlorine, chloride of lime, or permanganate of potash. By the action of hydrogen peroxide in presence of ammonia on pararosaniline, diamidobenzophenon is formed.\*

Under the influence of reducing agents, rosaniline loses oxygen, and is converted into *leucorosaniline*:  $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O} + 2\text{H} = \text{C}_{20}\text{H}_{21}\text{N}_3 + \text{H}_2\text{O}$ .

The constitution of *leucorosaniline hydrochloride* is shown by the formula—



Leucorosaniline and its salts are colourless, as is indicated by the name (see p. 457). Leucorosaniline is stable in the air; by moderately strong oxidising agents it is reconverted into rosaniline. Rosaniline in the free state is colourless, and its colouring character appears only when it combines with one equivalent of acid to form a salt like  $\text{C}_{20}\text{H}_{20}\text{N}_3\text{Cl}$ . It forms also diacid and triacid salts. The polyacid salts, especially the triacid salts, like  $\text{C}_{20}\text{H}_{19}\text{N}_3(\text{HCl})_3$ , are very soluble in water, and are colourless or of a brownish-yellow colour,

\* G. v. Georgievics, *Journ. Soc. Dyers and Col.*, 1905, p. 141.

both in the solid or dissolved state, and when fixed on the fibre. The polyacid salts are dissociated by water, forming monacid salts and free acid. The monacid salts of rosaniline, which consist of one equivalent of rosaniline and one equivalent of acid, like  $C_{20}H_{19}N_3$ , HCl, form crystals which have a metallic green lustre in reflected light; in transmitted light and in thin layers they are red; the solutions are crimson-red, and show no fluorescence.

Neither rosaniline nor the rosaniline salts are poisonous.

*Rosanilins hydrochloride*,  $C_{20}H_{19}N_3$ , HCl, forms rhombic crystals, which are sparingly soluble in pure water, but more readily in acidulated water or in alcohol, also amyl alcohol. The crystals absorb moisture from the air. With strong hydrochloric acid they form the triacid salt mentioned above, which is decomposed into the original salt when mixed with an excess of water.

*Rosaniline acetate*,  $C_{20}H_{19}N_3$ ,  $C_2H_3O_2$ , is the most soluble rosaniline salt; it forms large green crystals, which become brownish-red after some time.

In addition to these two salts rosaniline nitrate,  $C_{20}H_{19}N_3$ ,  $HNO_3$ , and rosaniline sulphate,  $(C_{20}H_{19}O_3)_2$ ,  $H_2SO_4$ , are sometimes brought into commerce.

*Commercial Magenta* is obtained on the large scale by the oxidation of the so-called *aniline-oil for red* which is a mixture of aniline, orthotoluidine, and paratoluidine; the presence of a certain amount of paratoluidine in this mixture is necessary. The oxidising agents employed are arsenic acid (arsenic acid-process) or nitrotoluene in the presence of iron and hydrochloric acid (nitrobenzene-process). The former method has been almost relinquished and Magenta is now manufactured almost exclusively by the nitrobenzene-process. The crude product contains, in addition to rosaniline and pararosaniline, Phosphine and a number of inferior dyestuffs; it is purified by crystallisation, and the crystals are selected and separated according to purity; the mother liquors yield inferior qualities. In this way the various brands of commerce are obtained.

**Magenta, blue shade** (extra, double refined, diamond, Rubine), is almost pure hydrochloride of rosaniline (and pararosaniline), nearly free from Phosphine or other dyestuffs.

**Magenta, yellow shade**, contains some Phosphine. It is not easily distinguished by its appearance from the blue shade of Magenta; by a dye-trial the difference at once becomes apparent.

*Impure products*, which contain more Phosphine, and, in addition, brownish colouring matters, are brought into commerce as amorphous powders or lumps of irregular shape, and sold under various names, as *Cerise*, *Grenadine*, *Cardinal*, *Amaranth*, *Geranium*, *Russian Red*, *Maroon*, &c.

Commercial Magenta forms green crystalline masses or powders with a metallic lustre; good qualities are always well crystallised and dissolve without leaving any considerable residue in pure water, but more readily in slightly acidulated water. The solution is almost entirely decolourised by sulphur dioxide, whereas impure samples remain dark yellow to brown when treated with this reagent. If the sample is pure the rosaniline-base is precipitated from the solution in a colourless state.

Magenta shows the following general reactions:—It dissolves in water with a bluish-red colour; hydrochloric acid turns the colour of the aqueous solution an orange-yellow; the original colour is restored by sodium acetate. Caustic soda precipitates from the aqueous solution a more or less reddish precipitate, readily soluble in alcohol. In concentrated sulphuric acid Magenta dissolves with a brownish-yellow colour; the solution becomes nearly colourless on dilution with water.

Magenta is tested by comparative dye-trials. For the detection of arsenic in Magenta a sample is incinerated with soda ash and the residue tested by Marsh's test, or it is distilled with hydrochloric acid and ferrous chloride,

and examined in Marsh's apparatus. In order to estimate arsenic quantitatively, Magenta is fused with nitre and soda ash and the quantity of arsenic estimated by means of magnesia mixture in the form of magnesium ammonium arsenate.

*Applications.*—Magenta is used for the dyeing of the textile fibres, and for other materials, such as leather, paper, &c. To dissolve the crystals more readily they are ground to a powder and moistened with methylated spirits; a great quantity of water (200 to 300 parts) is required for the solution of the dyestuff; and, if the solution has been allowed to stand for some time after filtering, it should be carefully examined in order to see if any crystals have been formed. Magenta dyes bright and pure bluish-red shades on the various fibres. The shade obtained on tannin mordanted cotton is not nearly so bright as on wool or silk.

Cotton can be dyed with Magenta according to the various methods described for the basic colours. The most permanent shades are obtained on material prepared with tannin and metallic fixing agents (antimony, tin, &c.).

Cotton is mordanted with tannin and antimony or with tannin and stannic salt, and dyed in a fresh tepid bath for 45 to 60 minutes. For a full shade about 1 per cent. of dyestuff (of the weight of the material) is required. To ensure level dyeing the colour solution is added gradually. The bath is exhausted if small quantities of dyestuff are employed. After dyeing the cotton is dried without washing. The bluish-red thus obtained is fairly fast to soaping but not to light. Mordanting with Turkey-red oil or soap and aluminium salts, and dyeing as on tannin-mordants, yields brighter though loose shades. Magenta can also be fixed on cotton with albumen, but this process is altogether too expensive. Unmordanted cotton can also be dyed by being worked in a strong solution of Magenta, to which, towards the end of the operation, some alum is added; the colour is readily stripped from the fibre by soaping and even by rinsing in water. This method is sometimes employed for producing bright tints on bleached calico, but only in cases where fastness is not required. It is said that the Chinese peasants use Magenta and other colours in this way, even without adding any alum.

It has been previously mentioned that the direct cotton colours can be topped with Magenta.

Wool is dyed with Magenta without any preparation after scouring. The bath is slightly acidulated with acetic or sulphuric acid; sulphuric acid makes the shade more bluish than acetic acid. An addition of a quantity of magnesium sulphate (8 per cent.), or zinc sulphate (6 per cent.), or alum (3 per cent.), or Glaubersalt (20 per cent. of the weight of the wool), causes the colour to go on to the fibre more evenly and gives more brightness to the shade. The wool is dyed in a boiling bath with or without any of these additions; the boiling is continued for 15 to 20 minutes, and then the temperature is allowed to fall to 60° or 70° C., as indicated in the introduction to the basic colours (p. 462). The shade is not fast to light or to milling.

Magenta is not dyed on wool as much as formerly, having been replaced by acid colours.

Silk is dyed with Magenta in a fresh soap-bath containing 1½ to 2 per cent. of neutral soap (of the weight of the silk). The liquor should lather slightly when stirred up, and, if the surface of the bath becomes bronzy during the dyeing, soap must be added until the bronze scum disappears. Turn the silk at first three times in the soap-bath; then add the colour by degrees in small quantities, and turn the silk while raising the temperature to 70° or 80°. Take the silk out when the desired shade is obtained, rinse well,

brighten with acetic or tartaric acid, and dry. Mineral acids in the brightening bath produce a bluer shade, which is liable to change on exposure to the air. Magenta can also be dyed on silk in an acid bath: wash the silk in tepid water to remove any soap, and dye in a warm bath containing acetic or tartaric acid; add the colour gradually until the desired shade is obtained, and dry without washing.

**IMPURE MAGENTAS: CERISE, GRENADINE, CARDINAL, AMARANTH, GERANIUM, RUSSIAN RED, MAROON, &c.**—These are products prepared from the mother liquors of Magenta crystals; and consist of mixtures of salts of Rosaniline, Pararosaniline, Phosphine, Chrysaniline, Mauvaniline, Violaniline, &c. They all yield duller and more yellowish shades than Magenta, and are used for their comparative richness of colour, not for the brilliancy and purity of their shades.

The impure Magentas are applied in dyeing exactly like Magenta; but the solutions should be filtered with great care before use, since they contain much tarry matter. Like Magenta they are not fast to light.

*Cerise, Grenadine, &c.*, are amorphous brown masses with a vitreous fracture, or powders of a brown colour, and mainly consist of Magenta and Phosphine. They dye a yellowish to brownish-red.

*Cardinal, Amaranth, Geranium, and Russian Red* are similar mixtures of inferior quality.

*Maroon (Chestnut-brown, Bordeaux for cotton, Crimson)* is also obtained from the mother liquors of Magenta. It is met with in commerce as a powder or paste or in lumps. If not readily soluble in water it may be dissolved with the aid of a little hydrochloric acid. In alcohol it is freely soluble.

Maroon dyes from red-brown to dark claret shades and is applied in the same way as Magenta. Silk is dyed in boiled-off liquor.

**NEW MAGENTA (M.L.B., Oehler-Griesheim). ISORUBINE (Berlin).**  
 $C_{22}H_{24}N_3Cl$ .

This product is obtained by the condensation of diamidoditolylmethane and orthotoluidine. It is the salt of a trimethylpararosaniline, and is analogously constituted to Magenta, which it resembles in character and dyeing properties; it has, however, the advantage of better solubility, and does not tend to separate as crystals from its aqueous solution. New Magenta forms a green powder which is soluble in water with a bluish-red colour. The solution is turned yellow by excess of hydrochloric acid, but becomes red again on diluting with water. Caustic soda decolourises the solution, and produces a dirty red precipitate of the base. The dyestuff dissolves in concentrated sulphuric acid with a yellowish-brown colour; the solution becomes yellowish-brown to red on diluting, according to the quantity of water that is added.

*Application.*—New Magenta is employed like ordinary Magenta on the various textile fibres; the shade is slightly bluer.

**RHODAMINE. ROSAZEÏNE, ANISOLINE, RHODINE, IRISAMINE, SAFRANILINE.**

The various kinds of Rhodamines (although basic dyestuffs) are chemically related to the Eosins, and will be fully treated in a special chapter, together with those colours.

**PYRONINE G,  $C_{17}H_{19}N_2OCl$  (Leonhardt).**

Pyronine G is obtained by the oxidation of tetramethyldiamidophenylmethaneoxide. The last-named compound is prepared by the condensation of formaldehyde with dimethylmetamidophenol.

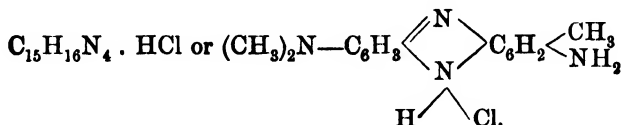
Green glittering crystals; aqueous and alcoholic solution, red, with a yellow fluorescence; HCl, orange solution; NaOH, pale red precipitate; solution in  $H_2SO_4$ , reddish-yellow; on diluting, redder.

Pyronine dyes a brilliant very bluish-red similar to safflower-pink.

Cotton is mordanted with tannin and antimony, and dyed with  $\frac{1}{2}$  to 2 per cent. of Pyronine, in the same way as Magenta. The shade is distinguished by unusual fastness to soaping. For wool this dyestuff is not suitable. Silk is dyed with Pyronine in a neutral soap-bath, in the same way as Magenta.

**ACRIDINE RED 3 B** (Leonhardt).—This dyestuff is produced by oxidising the above-mentioned Pyronine. It is employed in the same manner and yields fine red shades, slightly yellower than those of Pyronine.

**NEUTRAL RED** (Cassella) (**TOLUYLENE-RED**),\*



Neutral red is the hydrochloride of dimethyldiamidotoluphenazine, obtained by the action of nitrosodimethylaniline hydrochloride on metatoluylenediamine. The base of the dyestuff forms salts, with one, two, or three equivalents of acid; the monacid salts only are stable in aqueous solutions.

Neutral red forms an olive-black powder, which is readily soluble in water with a claret-red colour; the alcoholic solution is Magenta-red with a brown-red fluorescence. The aqueous solution is turned from violet to blue by hydrochloric acid, while caustic soda produces a brownish precipitate. The solution of Neutral red in sulphuric acid is green, and becomes, on diluting with water, at first blue and gradually bluish-red.

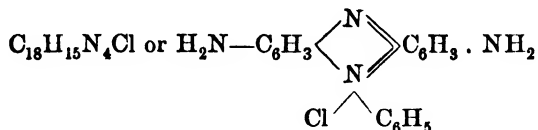
Cotton is mordanted with tannin and antimony and dyed with Neutral red in a fresh neutral bath; the material is entered at the ordinary temperature and the bath heated slowly to 50°.

Neutral red yields a dull bluish-red shade, which is not fast to light.

Wool and silk are not dyed with Neutral red.

#### SAFRANINE.

Various brands of Safranines are manufactured, which consist of the mixtures of the hydrochlorides of various isomeric and homologous bases. The simplest representative of these is *para-amidophenyl para-amidophenazonium chloride* or *Phenosafranine*,



The Safranines form salts with one, two, or three equivalents of acids; the monacid salts only are stable in solutions. By caustic soda the dyestuffs are precipitated, but the base is not separated in the free state thereby. Reducing agents form colourless *leucosafranines*, from which the dyestuffs are regenerated on oxidation by the air. The Safranines dissolve in sulphuric acid with a green colour; the solution becomes first blue, then violet, and finally red on diluting with water (general reaction of the Safranines).

*Phenosafranine* is obtained by the oxidation of a mixture of one equivalent of paraphenylenediamine and two equivalents of aniline.

It forms green glittering crystals, which dissolve in water with a red

\* The position of the double bindings of the azine, thiazine, and acridine dyestuffs is uncertain, as it is not definitely known whether they are orthoquinonoid or paraquinonoid compounds.

colour. The dyestuff resembles ordinary Safranine in properties and application, except that the shade is more bluish.

*Ordinary Safranine.*—This dyestuff consists of a mixture of pheno- and toluosafranines. For its production aniline-oil (such as contains chiefly ortho-toluidine) is converted with sodium nitrite and hydrochloric acid into amido-azo-compounds; the product is reduced with zinc and hydrochloric acid, and a mixture is obtained of toluylenediamine, orthotoluidine, and various homologous bases, certain quantities of ortho- or paratoluidine or aniline are added, and the mixture is subjected to oxidation by means of potassium bichromate.

According to the composition of the materials—whether they contain more or less aniline or the one or other toluidine—the composition of the product varies slightly, and the shade becomes more bluish or more yellowish; the differences, however, are small, and the properties generally remain the same.

*Ordinary Safranine* is generally a red-brown powder, which is readily soluble in water and in alcohol with a red colour; the aqueous, and especially the alcoholic, solution shows a fine yellow fluorescence. Hydrochloric acid turns the aqueous solution blue-violet and caustic soda causes a brown-red precipitate. With sulphuric acid the general reaction of the Safranines (green solution, &c., p. 469) is obtained.

*Application of the Safranines—Cotton.*—The best results in dyeing cotton with the various Safranines are obtained by previously mordanting with tannin and antimony and dyeing in a fresh bath; enter cold and heat slowly, not beyond 60°; add the dyestuff by degrees; a little acetic acid in the dye-bath makes the colours brighter. The shades are very fast to soaping, and moderately fast to light. Stannic chloride, basic alum, or lead acetate can be used instead of antimony for fixing the tannin; but the shades thus obtained are inferior in fastness and purity. Very light shades can be dyed in a soap-bath without previous mordanting; but they are not at all fast to washing or to light.

Wool can be dyed with Safranine in a neutral, acid, or alkaline bath; the colour is not fast to light, fading considerably within 24 hours. The dyestuff is sometimes added to reduced indigo to produce redder shades in the vat.

Silk is dyed in a bath of neutral soap. Prepare the bath with the dyestuff, enter the silk at 20° to 25° C. and heat to 50° or 60°; turn until the desired shade is obtained; wash and brighten in tartaric or acetic acid and dry. Brightening with sulphuric acid makes the shade bluer.

**AZINE SCARLET G (M.L.B.)** belongs to the group of Safranines, and dyes more yellowish shades of red than these.

**RHODULINE RED** and **BRILLIANT RHODULINE RED B (Bayer).**—These dyestuffs are also nearly related to the Safranines, and yield similar shades of great brightness and the same fastness.

**MAGDALA RED, NAPHTHALENE RED, or NAPHTHYLAMINE PINK (Durand).**  $C_{30}H_{21}N_4Cl$  and  $C_{30}H_{20}N_3Cl$ .

This dyestuff is a mixture of a Safranine of the naphthalene series and of a similar product, containing one amino-group less, and is constituted analogously to Phenosafranine. It is prepared similarly to the ordinary Safranine by reducing amidoazonaphthalene (from alphanaphthylamine) and oxidising the product after one equivalent of alphanaphthylamine has been added. The yield is low, and thus the price of Magdala red is very high.

Magdala red is a dark brown powder, not soluble in cold and sparingly soluble in hot water. It dissolves freely in alcohol with a cherry-red colour and a strong cinnabar-red fluorescence; by this property it is best recognised, as only some derivatives of Resorcin, such as diazoresorufin, resemble it in this respect; the latter differ, however, from it in their behaviour towards caustic

alkalies. Hydrochloric acid makes the solution of Magdala red more bluish; caustic soda causes a red-violet precipitate. The solution in sulphuric acid is greyish-blue, and turns bluish-red on dilution with water. Magdala red on reduction is converted into a leuco-compound from which the dyestuff is regenerated on oxidation by the air.

*Application.*—Magdala red, on account of its high price, is used in small quantities only, and exclusively in silk dyeing. It yields a beautiful pink with a strong fluorescence, which is especially fine on velvet. It loses the brilliancy in deep shades, and these are produced better and cheaper with other colours—*e.g.*, the Eosins and Rhodamines.

One part of dyestuff produces a light pink on 1,000 parts of silk. Dye in a bath with neutral soap or boiled-off liquor; enter cold, and raise to 50° or 60°; brighten with acetic acid.

Magdala red is faster than most of the basic colours to light, acids, and alkalies.

#### JANUS RED B and JANUS BORDEAUX B (M.L.B.).

Janus red B and Janus Bordeaux B are basic azo-colours possessing the general dyeing properties belonging to this group (see pp. 462 and 464). They yield red or claret shades of good fastness to washing, but not very fast to light.

#### CHRYSOÏDINE. $C_{12}H_{12}N_4 \cdot HCl$ or $C_6H_5N_2C_6H_3(NH_2)_2HCl$ .

Chrysoïdine or *diamidoazobenzene chloride* is formed by the action of diazobenzene chloride on metaphenylene diamine. A homologous dyestuff, also called Chrysoïdine, is produced from diazotoluene and toluylene diamine. *Cardinal red* and *Magenta scarlet* are mixtures of Magenta and Chrysoïdine; under the names of *Cotton-scarlet* or *Cotton-ponceau* mixtures of Safranine and Chrysoïdine are sold.

The base of Chrysoïdine ( $C_{12}H_{12}N_4$ ) forms salts with one and with two equivalents of acids; the monacid salts only are stable in aqueous solutions.

Chrysoïdine is sold in the form of a red-brown crystalline powder or black crystals having a green metallic reflex. It dissolves freely in water with an orange colour. Hydrochloric acid produces in the aqueous solution an orange-coloured and soluble gelatinous precipitate; caustic soda forms a yellow precipitate. Sulphuric acid dissolves it with a brownish-yellow colour; the solution becomes orange on dilution with water. Chrysoïdine, being an azo-compound, is decolourised by reducing agents, but is not regenerated by oxidation.

*Application.*—Chrysoïdine is not used much on silk and still less on wool; it is not very suitable for printing, since it does not stand the influence of steaming.

Cotton can be dyed with Chrysoïdine in light shades without any mordanting and without any additions to the dye-bath. For deep shades mordanting with tannin is required. A pure red-orange shade is obtained, which is not fast to light or to washing.

Very good bistre-shades are produced by padding unmordanted cotton cloth with Chrysoïdine and passing through a solution of diazotised *p*-nitraniline. The colour is fast to washing and may be discharged by sodium formaldehyde-sulphoxylate (hydrosulphite formaldehyde).

Silk.—Dye in a weak soap-bath for half an hour at 50° to 60°, wash and brighten with acetic, tartaric, or sulphuric acid, wring and dry.

#### TANNIN ORANGE R (Cassella).

Tannin orange R is a basic azo-dyestuff produced by the action of diazotised *p*-amidobenzylidimethylamine on betanaphthol.

The commercial product forms a brown paste or powder, soluble in water and in alcohol with a brown colour. Hydrochloric acid and caustic soda



produce brown precipitates in the aqueous solution. The solution in sulphuric acid is cherry-red, and on diluting it yields an orange-brown precipitate.

*Application and Properties.*—Tannin orange R dyes a very bright orange, and may be used with advantage in place of Chrysoidine, as it yields much faster colours on cotton mordanted with tannin and antimony, the shades being fairly fast to soap, light, and acids. It is especially valuable for calico-printing.

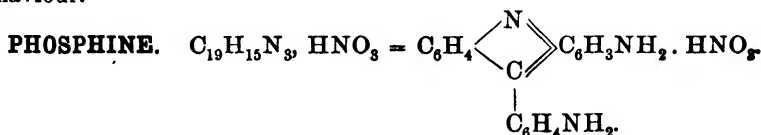
#### NEW PHOSPHINE G (Cassella).

This also is a basic azo-dyestuff obtained by the action of the same diazo-compound as used for Tannin orange R on resorcin.

It forms a yellow-brown powder, soluble with a yellow-brown colour. The aqueous solution is not altered by hydrochloric acid, and becomes redder and darker on addition of caustic soda. The solution in sulphuric acid is yellow-brown and not changed by diluting with water.

*Application and Properties.*—New Phosphine G is chiefly dyed on cotton mordanted with tannin and antimony, and yields a good Nankin yellow of fairly good fastness to washing and soaping. The dyestuff is chiefly used for printing on cotton, satin, and unions.

**AZOPHOSPHINE G O (M.L.B.)** is a dyestuff of similar constitution and behaviour.



#### Chrysaniline, Aniline orange, Leather yellow, Philadelphia yellow, &c.

Commercial Phosphine is not a uniform substance; it is a mixture of the nitrates of *diamidophenylacridine* and of homologous bases. Diamidophenylacridine ( $C_{19}H_{15}N_3$ ) is also called *parachrysaniline*; the next homologous base *chrysaniline* ( $C_{20}H_{17}N_3$ ) is also present in commercial Phosphine. (See also *Impure magentas*.)

Phosphine is produced from the resinous bye-products and mother liquors of Magenta. It comes into commerce as the nitrate (or hydrochloride), which forms a yellow or orange powder, readily soluble in water with an orange-yellow colour and a yellow-green fluorescence. The aqueous solution is not altered by hydrochloric acid; caustic soda produces therein a yellow flocculent precipitate. Sulphuric acid dissolves Phosphine with a light yellow colour and a green fluorescence; the solution becomes deeper yellow on dilution with water.

*Application.*—Phosphine is dyed exactly in the same way as Magenta and Safranine. It is a very costly dyestuff, and is now chiefly used in leather dyeing. The commercial articles differ greatly in quality.

Cotton is dyed on tannin mordant which has been fixed with antimony; a Nankin-yellow shade is obtained, which possesses considerable fastness to soap, but not to light.

Wool may be dyed with Phosphine in a hot bath which is slightly acidulated with acetic acid. The dyestuff, however, is hardly used on wool, except in printing.

Silk is dyed with Phosphine exactly as with Safranine.

**PATENT PHOSPHINE** (Ch. Ind. Basle), **HOMOPHOSPHINE** (Leonhardt), **PARAPHOSPHINE** and **DIAMONDPHOSPHINE** (Cassella), **RHEONINE** (B.A.S.F.), **FLAVOPHOSPHINE** (M.L.B.), **AUROPHOSPHINE** (Berlin) are dyestuffs of similar composition and behaviour as ordinary Phosphine; they are, however, not bye-products of the Magenta-melt, but special synthetic products of the acridine series. They are chiefly used for dyeing cotton and leather

like Phosphine, and yield yellow and orange shades of little fastness to light and fairly good fastness to soaping.

**ACRIDINE ORANGE N O** (Leonhardt).  $C_{17}H_{19}N_3 \cdot HCl + ZnCl_2$ .

Acridine orange is the double salt of zinc chloride and the hydrochloride of *tetramethyldiamidoacridine*; the leuco-compound is produced by heating tetramethyltetraamidodiphenylmethane with acids and is subsequently converted into the colour-base by oxidation. Acridine orange is sold as an orange-coloured powder which dissolves in water and in alcohol with an orange colour and a greenish fluorescence. The aqueous solution is turned red on addition of hydrochloric acid, and gives a yellow precipitate with caustic soda. The solution in concentrated sulphuric acid is almost colourless with a greenish fluorescence, and becomes at first red and then orange on dilution with water.

*Application.*—Acridine orange gives orange shades, which are very fast to soaping. It is recommended for the dyeing of leather, which material acquires a peculiar golden lustre thereby.

**Cotton** is mordanted, as usual, with tannin and antimony, and dyed with the addition of 2 grms. (3 ozs.) of alum per litre (10 galls.) of the dye-liquor. The colour gives good results in dyeing and printing.

**Silk** is dyed in a soap-bath broken with acetic acid; the shade shows a fine greenish fluorescence.

Similar brands are:—**ACRIDINE ORANGE G G, NEW ACRIDINE ORANGE R, ACRIDINE GOLDEN YELLOW.**

**BENZOFLAVINE** (Oehler).  $C_{21}H_{19}N_3 \cdot HCl$ .

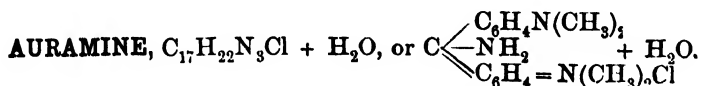
Benzoflavine is *diamidodimethylphenylacridine*; it is produced by condensing benzaldehyde with two equivalents of metatoluylenediamine and oxidising the intermediary product, hydrodiamidodimethylphenylacridine (the leuco-compound), with ferric chloride.

Benzoflavine is sold as a brownish-orange coloured powder, which dissolves sparingly in cold water, better in hot water, with a yellow colour and a yellowish-green fluorescence. The alcoholic solution is reddish-yellow and shows a green fluorescence. The aqueous solution gives an orange precipitate on addition of hydrochloric acid and a yellowish-white precipitate with caustic soda. Sulphuric acid dissolves the product with a greenish-yellow colour and a very strong green fluorescence; on dilution with water, at first, a yellowish solution and, then, an orange precipitate is formed.

*Application.*—Benzoflavine is applied on cotton in the same way as the other basic dyestuffs; it is not of much importance in wool and silk dyeing. Dissolve by stirring 1 part of dyestuff in 100 parts of boiling water to which 3 parts acetic acid have been added; boil for fifteen minutes. Add the solution to the dye-bath through a fine hair-sieve. Cold solutions must be heated up and filtered before use.

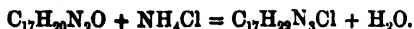
**Cotton** may be dyed with or without mordanting. Enter the cotton, which has been mordanted with tannin and antimony, into the lukewarm bath, and heat to 80°; the temperature may, however, be raised to boiling without injury to the colour. A pure yellow shade is obtained, which is fairly fast to soap and light.

Benzoflavine is especially valuable in calico-printing, since it is not so sensitive to high temperatures, acids, and chlorine, as Auramine.



Auramine or *aminotetramethyldiaminodiphenylmethane chloride* is formed

by condensing tetramethyldiamidobenzophenone and ammonium chloride with the aid of zinc chloride :



Auramine is offered to the trade in pure quality as Auramine O ; in addition some brands, containing more or less dextrin, are found in the market under the names Auramine I., II., or III.

Auramine forms a yellow powder, which is sparingly soluble with a light yellow colour in cold, but freely soluble in hot water, or acidulated water. The aqueous solution is decomposed on boiling or prolonged standing into the constituents from which Auramine is prepared, which decomposition takes place more rapidly in acid than in neutral solutions. The aqueous solution becomes darker on addition of hydrochloric acid and gives a white precipitate with caustic soda. The solution in sulphuric acid is colourless and is turned a light yellow on dilution with water.

*Application.*—Auramine is valuable for shading other basic colours, such as Magenta, Safranine, and the greens. It should be dissolved in hot water, which, however, must not be heated over 80°, neither must the temperature of the dye-bath be raised above this point. If it should be necessary to acidify the bath, acetic acid must be used, not mineral acids, Auramine being easily decomposed by the latter.

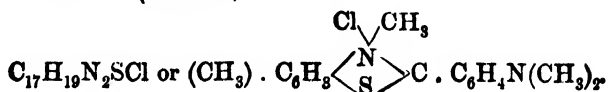
Cotton is mordanted in the usual manner with tannin and antimony ; for light shades the use of small quantities of mordanting materials is advisable when it is desired to obtain a pure yellow—i.e., one which is not reddish in tone. The mordanted cotton should be worked for twenty to thirty minutes in a weak soap-bath [ $1\frac{1}{2}$  grms. ( $2\frac{1}{2}$  ozs.) neutral soap per litre (10 galls.)] and then rinsed thoroughly in water before it is dyed. Dye in a fresh lukewarm bath, wring and dry at the usual drying temperatures ; if necessary the dye-bath may be heated to 80°, but not higher. In printing, the colour must not be steamed under pressure. Auramine on tannin and antimony is fairly fast to soap and moderately fast to light, but very sensitive to chlorine. When dyed alone it gives a pure yellow ; it possesses importance in cotton dyeing for the production of compound shades.

Wool is dyed in a neutral bath or in a soap-bath containing 2 to 5 grms. soap per litre (3 to 8 ozs. per 10 galls.) for half an hour at 35° to 70°, and for the production of very bright yellows stoved after dyeing, whereby the shade becomes more brilliant. It yields a brighter yellow than the acid yellows, and together with Rhodamine very fine oranges. It is, however, suitable only if stress is laid on brightness without regard to fastness of shade.

Silk is dyed in a neutral bath or with a little neutral soap at 60° to 70°. The colour must be added gradually and the silk be turned very quickly. After dyeing and rinsing the goods are brightened with a small amount only of acetic acid, on account of the sensitiveness of Auramine to acids. Silk is rarely dyed with Auramine.

**AURAMINE G** (Ch. Ind. Basle, B.A.S.F., Geigy).—This dyestuff is chemically related to ordinary Auramine and closely resembles it in behaviour, but for its more greenish-yellow shade.

**THIOFLAVINE T** (Cassella).



Thioflavine T is related by its chemical constitution to Thioflavine S, a yellow direct cotton colour. Thioflavine T is *dimethyldehydrothiolutidine*

*methyl chloride* and is produced by heating dehydrothiitoluidine with methyl alcohol and hydrochloric acid in closed vessels to 170° C.

Thioflavine T is an orange-yellow powder, which dissolves in water and in alcohol with a yellow colour; the alcoholic solution shows a greenish fluorescence. Hydrochloric acid does not alter the appearance of the aqueous solution; caustic soda produces a yellow precipitate. The solution in sulphuric acid is colourless and shows a dark green fluorescence; on dilution with water a light yellow solution is obtained.

*Application.*—Thioflavine T yields pure greenish-yellow shades, and is a very useful dyestuff for the various fibres. It is employed with advantage for shading other basic colours, since it is not sensitive to high temperatures and resists well the action of acids and chlorine.

Cotton is mordanted with tannin and antimony, and dyed like the other basic dyestuffs. The temperature may be raised to boiling. The colour is fairly fast to soap and light.

Wool is dyed in a bath which may be slightly acidulated with acetic acid. Enter at about 40°, heat to 80° to 90° or to boiling, and maintain so for twenty or thirty minutes. It may also be dyed in a soap-bath and stoved after dyeing, like Auramine, in which way very fine greenish-yellow shades are obtained.

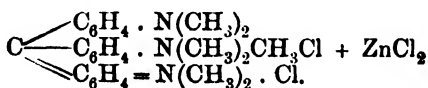
Silk is dyed in a boiling soap-bath and brightened with sulphuric acid. The shade possesses a green fluorescence.

**JANUS YELLOW G and R (M.L.B.).**—These two dyestuffs are complicated azo-compounds of basic character which dye both unmordanted and mordanted cotton.

Brownish powder which dissolves in water with a yellow colour. Hydrochloric acid makes the colour of the solution more intense; caustic soda produces a brown precipitate. The solution in sulphuric acid is magenta-red, and becomes yellowish-brown on dilution. By reduction with zinc dust and hydrochloric acid the colour is permanently destroyed.

*Application.*—Like the other Janus colours (see pp. 462 and 464) for cotton, unions, and satins, Janus yellow G dyes a slightly reddish, not very bright yellow, moderately fast to light and good to alkalies. Janus yellow R dyes a brighter, rather reddish yellow fairly fast to light, but is reddened by alkalies. Both are fairly fast to washing and acids when dyed on a tannin-mordant on cotton.

**METHYL GREEN.**  $C_{26}H_{33}N_3Cl_2 + ZnCl_2 =$



**Light-green. Vert Etincelle. Vert de Methylaniline.**

This product is a chloromethylated Methyl violet and is manufactured by the action of methyl chloride on Methyl violet. A more bluish-green dyestuff is prepared by using ethyl bromide instead of methyl chloride.

By the action of methyl or ethyl chloride, bromide or iodide, &c., on Rosaniline and on Hofmann's violet similar green colouring matters were formerly produced—*e.g.*, *Iodine green*, *Bright green*, or *Vert lumière*. These were the first green aniline colours prepared; they have long disappeared from the market, having been replaced, first, by the cheaper Methyl green and, later, by the Benzaldehyde greens.

Methyl green is sold either in small green crystals with a golden lustre or as a light green powder. It dissolves readily, with a bluish-green colour, in water and in alcohol, but not in amyl alcohol (distinction from Benzaldehyde green). The aqueous solution is turned reddish-yellow by hydrochloric acid

an unstable triacid salt being formed; hence the colour becomes yellowish-green on dilution with water. Caustic soda decolourises the aqueous solution, liberating the soluble colour base in the free state. Methyl green dissolves with a reddish-yellow colour in sulphuric acid; the solution becomes green on dilution with water. When heated over 100° C., Methyl green is decomposed into Methyl violet and methyl chloride.

Solutions of Methyl green yield, on addition of Picric acid a dark green crystalline precipitate, which is nearly insoluble in water, but readily soluble in alcohol; it was sold for a time as *Spirit-soluble green*.

Methyl green should be entirely soluble in water with a bluish-green colour.

*Application.*—Methyl green is still used to some extent on silk, because it can be shaded better than the other green dyestuffs with Picric acid. For the dyeing of cotton and wool it has been replaced by Benzaldehyde green, Brilliant green, Acid green, &c., since these dyestuffs require no mordant on wool, are not altered by heat, and are better suited for compound shades. Methyl green, however, does not rub so much as Malachite green. In dyeing with Methyl green the bath should never be heated to the boiling point, copper vessels must be avoided, and calcareous water should be slightly acidulated.

Cotton is mordanted with tannin and antimony and dyed in a bath the temperature of which may be raised to 50°. First, two-thirds of the required amount of dyestuff are added and the rest after twenty minutes dyeing. After washing, the goods are brightened in a weak acid bath. The shade is not fast to light.

Wool must be mordanted before dyeing with sodium thiosulphate. Both in mordanting and in dyeing, the wool must not come in contact with metals, such as copper, lead, or iron, that are liable to give rise to stains of metallic sulphides. Pipes which are coated with tin can be used for heating the dye-bath.

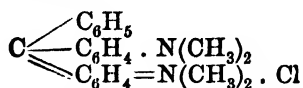
Dissolve for 100 kgs. (lbs.) wool, 20 kgs. (lbs.) of sodium thiosulphate, and 10 kgs. (lbs.) of alum; when all is dissolved add 4 kgs. (lbs.) of sulphuric acid. Enter the wool into the milky fluid at 40° and turn it for about one hour while the temperature is raised to 80° but not higher. Then wash the wool thoroughly in water, and pass it, after washing, through a bath containing a very small amount of ammonia. The ammonia bath may be dispensed with if 2 to 4 per cent. of borax or of acetate of soda are added to the dye-bath. Dye in a neutral bath or in one slightly acidulated with acetic acid at a temperature not exceeding 80°; wash and dry.

Silk is dyed in a lukewarm soap-bath, slightly acidulated with sulphuric or acetic acid. The temperature may be raised to 50°. After dyeing, the silk is washed and brightened with acetic or tartaric acid. If a yellower shade is desired Picric acid is added to the *brightening* bath, and the goods are dried at once and without rinsing, so as not to remove any Picric acid.

**MALACHITE GREEN.**  $C_{23}H_{25}N_2Cl$ , &c. (see below).

Benzal Green, Benzoyl Green, Victoria Green; Imperial, New, Solid or Diamond Green.

Malachite green is a derivative of diamidotriphenylmethane. It is obtained by first condensing benzaldehyde with dimethylaniline to form tetramethyl-diamidotriphenylmethane or leuco-malachite green; and, subsequently, oxidising this product into Malachite green:—



Chloride of Malachite green base.

Malachite green is sold in the form of several salts and double salts. It forms salts with one and with two equivalents of acids; the monacid salts only are stable compounds in aqueous solutions. The following two salts are commercial products known as Malachite green, &c. :—

1. *Oxalate*,  $2C_{23}H_{24}N_2 + 3C_2H_2O_4 + 2H_2O$ ; tablets with a metallic-green lustre.

2. *Zinc double chloride*,  $3C_{23}H_{24}N_2Cl + 2ZnCl_2 + 2H_2O$ , occurs either as prismatic crystals with a yellow beetle-green lustre or as a greenish powder.

These two salts are called without distinction by the same names in the trade.

Malachite green is soluble in water, in alcohol, and in amyl alcohol (thus differing from Methyl green), with a bluish-green colour. The aqueous solution becomes reddish-yellow on addition of hydrochloric acid; the original colour is restored on dilution with much water. Caustic soda produces in the aqueous solution a pale yellowish-green precipitate. Sulphuric acid dissolves the dyestuff with a yellow colour; on dilution with water the solution becomes at first orange then olive-green to bluish-green. Malachite green yields a leuco-product by reduction; the dyestuff is regenerated under the influence of strong oxidising agents, but not by the action of atmospheric oxygen.

*Application.*—Malachite green serves for the dyeing and printing of all fibres. Both forms, the oxalate and the zinc double salt, are used in precisely the same manner; in calico-printing, however, the oxalate is preferred, because zinc chloride may form precipitates with the tannin in the printing colour. The dyestuff is dissolved in hot water and filtered; calcareous water is corrected with acetic acid, for wool dyeing, with bisulphate of soda. Solutions of Malachite green should not come in contact with copper.

In dyeing with Malachite green the liquor can be heated to boiling without any risk (if Auramine has been added for shading purposes, the temperature, of course, must not be too high). The dye-bath is not exhausted. Malachite green yields intense shades of green, which are not fast to light, soaping, or milling.

Cotton is dyed, similarly with the other basic dyestuffs, after previously mordanting with tannin and antimony. Work the cotton for half an hour in a warm bath, which may be slightly acidulated with acetic acid, add the colour solution gradually, wring out, and dry without washing. By raising the temperature to the boil the shade loses in depth, but becomes brighter and faster to soaping; greater fastness to soaping is also obtained by drying the mordanted cotton before dyeing. A very light soaping of the dyed material brightens the shade. Tannin and basic alum, or basic alum alone, may be used for mordanting, or, for bright shades, Turkey-red oil and alum; the tannin-antimony method, however, is the best also for this dyestuff. Dark shades are produced with tannin and iron :—(1) Mordant with pyrolignite of iron (4° Tw.), oxidise by ageing, pass through weak limewater, wash, pass through solution of tannin, and dye as before; if the shade comes out too full it can be made lighter by passing the goods through a weak bath of stannous chloride. (2) Mordant first with tannin, and, subsequently, with pyrolignite of iron (6° Tw.), and dye as before. (3) Pad the material in a bath containing 1 part of tannin and 3 parts (by weight) of pyrolignite of iron (15° Tw.) in 100 parts of water; dry in the hot flue and dye as before.

Malachite green may be mixed, in cotton dyeing, with any of the basic colours. The direct cotton colours are very well adapted for shading this dyestuff and their use may save the mordanting operation. To obtain, for example, a yellower tone, dye first with Chrysophenin and top in a cold bath with Malachite green. A yellowish green can also be produced by mordanting

with alum; fixing with phosphate of soda; and dyeing, first, in Quercitron extract and, then, in Malachite green.

Wool is dyed with Malachite green either as such or after previous treatment with sodium thiosulphate.

(1) *Dyeing without previous treatment.*—The wool is dyed in a bath slightly acidified either with an acid (sulphuric, acetic, &c.) or with bisulphate of soda or sulphate of alumina. If the bath is not acid, it is imperfectly exhausted, and if the water is calcareous the exhaustion is even less complete. On the other hand, an excess of acid also prevents the bath from being exhausted; hence the bath should only just give an acid reaction. The wool is dyed at the boil for half an hour, washed, and dried.

(2) *Dyeing of Prepared Wool.*—The wool is prepared exactly as described for Methyl green and then dyed at the boil without any additions, washed and dried. This process is longer, and the wool acquires a peculiar appearance and smell; but it is necessary for the production of deep shades, while the colour becomes faster to light and milling and rubs less. A small quantity of basic alum in the dye-bath prevents felting of the wool and gives greater fastness to milling. The addition of soap to the dye-bath cannot be recommended in either case, because of the formation of sticky zinc soap if the double salt of zinc be used.

Silk is dyed in boiled-off liquor to which sulphuric acid has been added until the bath is only slightly alkaline. Heat the bath to 70° or 80°, add the colour solution and work the goods for half an hour, wash, brighten with a little acetic acid, and dry.

The basic or the acid colours may be used in the same bath with Malachite green, for shading purposes, both on wool and silk. If Malachite green is shaded with Picric acid, the goods should be dyed, first, with the green and, then, topped with Picric acid.

**BRILLIANT GREEN.**  $C_{27}H_{33}N_2 \cdot HSO_4$  or  $C_{27}H_{33}N_2 \cdot HC_2O_4 + H_2O$ .  
New Victoria Green, Ethyl Green, Fast Green J., Emerald Green.

Brilliant green is homologous with Malachite green, and is obtained when, in the manufacture, diethylaniline is substituted for dimethylaniline. The properties and modes of application are the same for both dyestuffs.

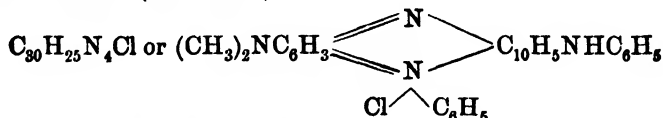
Brilliant green comes into commerce as the sulphate, which forms small crystals having a golden lustre; or as the oxalate, which crystallises in large prisms. The reactions are those of Malachite green; the solution is less bluish.

Brilliant green dyes a yellower and more brilliant shade than Malachite green.

**VICTORIA GREEN 3 B** or **NEW FAST GREEN 3 B.**  $C_{23}H_{23}N_2Cl_3$ .

This dyestuff is a chlorinated Malachite green, and is produced in a similar way from dichlorbenzaldehyde and dimethylaniline. It forms a green crystalline powder with a metallic lustre, which is little soluble in cold, more freely in hot water, and readily soluble in alcohol with a greenish-blue colour. The hot aqueous solution becomes gelatinous on cooling. Victoria green 3 B shows similar reactions as Malachite green, and is applied to the textile fibres in the same way as this dyestuff. It dyes a more bluish shade of green.

**AZINE GREEN** (Leonhardt).



Azine green or *anilidodimethylisorosinduline chloride* is produced by the action of nitrosodimethylaniline hydrochloride on (2 : 6) diphenylnaphthylene diamine.

Azine green is sold as a dark green powder, which dissolves in water and in

alcohol with a green colour. Both hydrochloric acid and caustic soda produce green precipitates in the aqueous solution. Sulphuric acid dissolves the dye-stuff with a brownish colour, which becomes green on dilution with water.

*Application.*—Azine green dyes a dark green, which is particularly adapted for cotton-dyeing and -printing. The colour is distinguished by relative fastness to soap and to light.

Cotton is mordanted as usual with tannin (5 to 10 per cent.) and antimony; dye in a fresh bath, enter cold, bring gradually to the boil, wash and dry. The dark green shade which is thus obtained is fairly fast to soaping and to light. On iron mordant the results are not so good as those obtained on tannin and antimony.

Silk is dyed with neutral soap; add the colour solution to the tepid bath, enter the material, bring to the boil, boil for one hour, wash, brighten with acetic acid, wash again, and dry.

**DIAZINE GREEN (Kalle). JANUS GREEN B (M.L.B.).**

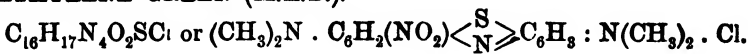
Azo-compound produced by the action of diazotised Safranin on dimethyl-aniline.

Brown or dark green powder, soluble in water with a blue colour. Hydrochloric acid produces a soluble blue precipitate in the aqueous solution, and caustic soda an insoluble black precipitate. The solution in sulphuric acid is olive green, and becomes, on dilution with water, blue. On reduction with zinc dust and hydrochloric acid the aqueous solution is decolourised, and by the action of air the pink colouration of Safranin is formed; the green is not regenerated.

*Application.*—The dyestuff may be used on mordanted or unmordanted cotton and union goods like the other azo-compounds of Safranin (see pp. 462 and 464), and yields dark shades of green. It is fairly fast to light, soap, and rubbing, and, therefore, may replace Malachite green in the case of dark green.

JANUS GREEN G (M.L.B.) is similar to the preceding brand, and yields purer shades of green.

**METHYLENE GREEN (M.L.B.).**

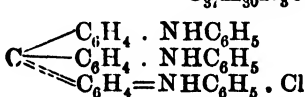
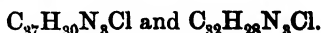


Methylene green is mononitromethylene blue or *mononitrotetramethylthionine chloride*. It is produced by the action of nitrous acid on Methylene blue. In its properties it resembles Methylene blue. By the action of reducing agents it yields amido-methylene blue, which resembles Methylene blue in shade.

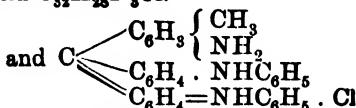
Methylene green forms a brown crystalline powder, which is soluble in water with a greenish-blue colour. Hydrochloric acid does not change the aqueous solution, caustic soda produces a dirty violet-brown precipitate. Sulphuric acid dissolves the dyestuff with a bluish-green colour, which becomes greenish-blue on diluting with water.

*Application.*—Methylene green is dyed on cotton mordanted with tannin and antimony, in the same way as Methylene blue (see p. 484), and is useful for compound shades. It dyes a full bluish-green shade, which resembles those produced with Methylene blue in fastness to light and soap.

**ROSANILINE BLUE or ANILINE BLUE, SOLUBLE IN SPIRIT.**



*Triphenylpararosaniline chloride.*



*Diphenylrosaniline chloride.*



Rosaniline blue is a phenylated Magenta, produced by heating rosaniline base in the presence of benzoic acid with a large excess of pure aniline (aniline for blue) to 180°. Rosaniline blue in the purest form is a salt of diphenylrosaniline containing varying amounts of triphenylpararosaniline salt, according to the composition of the Magenta from which it was prepared.

By reducing the quantity of aniline oil the material is not completely phenylated, so as to contain mono- and diphenylrosaniline; such products yield more or less dull and reddish-blue colours. The reddish shade of the inferior blues is particularly noticeable in artificial light, whereas the colour of the highest qualities appears as beautiful in artificial light as in daylight; hence the latter are called *Light blue* or *Night blue* (*Bleu lumière*; *Bleu de nuit*).

Rosaniline blue is brought into the market as the chloride, sulphate, or acetate, under the names of *Spirit blue*, *Base blue*, *Opal blue*, *Gentian blue 6 B*, *Hessian blue*, *Lyons blue*, *Light blue*, *Imperial blue*, *Humboldt blue*, *Parma blue*, or *Dahlia*.

Rosaniline blue forms salts with one, two, or three equivalents of acids; the monacid salts only are stable. It yields a leuco-compound *diphenyl-leucaniline* on reduction, which is readily reconverted into the blue dyestuff by oxidising agents.

Commercial Rosaniline blue is a brown, greyish-green, or violet-blue powder without a metallic lustre unless crystallised. It is not soluble in water and sparingly soluble in alcohol; the acetate is fairly soluble in alcohol, and is sometimes sold in solution. The alcoholic solution of Rosaniline blue has a beautiful blue colour, and is turned more greenish-blue by hydrochloric acid, red-brown by caustic soda. Sulphuric acid dissolves the dyestuff in the cold with a brownish-yellow colour; on dilution with water a flocculent blue precipitate is obtained.

*Application.*—The Rosaniline blues are not much used in cotton dyeing or printing, and to a limited extent only on wool; they are dyed on silk when a bright and very pure blue is demanded, such as cannot be obtained with the Soluble blues. The Rosaniline blues yield shades which are fairly fast to soaping and milling, but less so to light. They are now almost completely replaced by the Victoria blues, which are faster to milling, but less fast to light.

The Rosaniline blues are dissolved in 40 to 50 times their weight of methylated spirits, and the solution is gradually added to the dye-bath.

Cotton is best prepared with soap and aluminium acetate, as indicated on p. 461. The mordanted cotton is entered into a fresh lukewarm bath and the alcoholic solution of the colour is added very gradually, whilst the bath is slowly heated to the boil. After a good washing in water the process is completed by a final soaping in a weak soap-bath, to which so much acetic acid has been added as to make it slightly turbid.

Cotton can also be impregnated with soap only and then be dyed in a fresh bath, to which aluminium acetate has been added; or it may be mordanted with tannin and antimony, and dyed in a fresh bath containing alum.

Wool.—Prepare the bath with 5 per cent. of alum, 2 per cent. of sulphuric acid, and 1 per cent. of stannic chloride (of the weight of the wool); an addition of large quantities of common salt or Glaubersalt to the bath is advantageous. Turn the wool in the dye-bath, first at 60°, then add the alcoholic colour-solution gradually and bring to the boil; dye about 30 minutes, wash and dry.

Silk is dyed in a bath of boiled-off liquor which has been acidified with sulphuric acid; turn the silk in the lukewarm bath, then add the colour-solution gradually, and heat to the boil; wash and brighten with sulphuric acid.

Rosaniline blues, soluble in spirit, appear redder on silk than on wool; the difference is very considerable in artificial light, when the shade on wool is a pure blue, whereas that on silk appears decidedly violet.

**DIPHENYLAMINE BLUE.**  $C_{37}H_{30}N_3 \cdot Cl$ . Bavarian Blue.

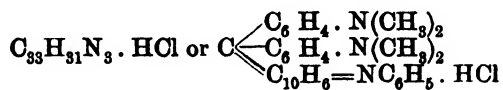
*Diphenylamine blue* or *triphenylpararosaniline chloride* is produced by heating diphenylamine with oxalic acid to  $130^\circ$ . It forms a brown powder insoluble in water and sparingly soluble in alcohol with a beautiful blue colour. It dissolves in sulphuric acid with a brownish-yellow colour; the solution yields a blue precipitate on diluting with water.

Diphenylamine blue, on account of its high price, is used in silk dyeing only. It gives a finer blue shade than Rosaniline blue or almost any other blue.

Methyl blue and Ethyl blue are methylated and ethylated diphenylamine blues.

*Applications.*—(See *Rosaniline blue.*)

**VICTORIA BLUE B** or **B S** (B.A.S.F., Ch. Ind. Basle, Sandoz).



Victoria blue B is the hydrochloride of *tetramethylphenyltriamidodiphenyl-naphthylcarbinol anhydride*, and is produced by the action of phenylalphanaphthylamine on tetramethyldiamidobenzophenone chloride.

Victoria blue B forms salts with one, two, or three equivalents of acid; only the monacid salts are stable. It yields a leuco-compound, and is regenerated therefrom by oxidising agents.

The commercial article forms a violet powder or a granular mass with a coppery reflex. It dissolves in warm water and in alcohol with a deep blue colour. The aqueous solution becomes turbid by continued boiling, the free colour-base being thrown down as a reddish resinous precipitate; acetic acid prevents this decomposition. In the presence of small quantities of mineral acids, Victoria blue does not dissolve as well as in pure water; large quantities, however, make it more soluble by forming diacid and triacid salts. Hydrochloric acid produces a blue precipitate in the aqueous solution, which re-dissolves on addition of more acid; the solution becomes at first green, then yellowish-brown, and contains the diacid and triacid salts. Caustic soda produces in the aqueous solution a red-brown precipitate. Sulphuric acid dissolves the dyestuff with a reddish-brown colour, which becomes yellow, olive-green, and blue on diluting with water.

*Application.*—Victoria blue B is employed on all fibres, and dyes a very bright and pure blue, which is fairly fast to soaping and milling and mild alkalies, but not fast to light.

In dyeing with Victoria blue, calcareous water must be corrected with acetic acid. It is advisable to proceed as follows:—The dry colour is mixed to a paste with acetic acid—about 750 c.c. ( $\frac{3}{4}$  pint) for 1 kg. (1 lb.) of dyestuff—and allowed to stand for some hours: hot water is then poured over the mixture, it is well stirred and the clear solution is filtered before use. The acetic acid has no injurious effect in dyeing.

Cotton is mordanted with tannin and antimony in the usual manner, and subsequently worked in a warm soap-bath, as described on p. 460. The soaping makes the ultimate shade purer and more even. Chromium mordant has been recommended for fixing the tannin, but it offers no advantages in dyeing, in calico-printing good results are obtained with chromium acetate (without tannin). Dye the mordanted cotton in a lukewarm bath, which contains for 10 kgs. (10 lbs.) of cotton 650 c.c. ( $\frac{3}{4}$  pint) of aluminium acetate ( $10^\circ$  Tw.); add the colour gradually, work the cotton thirty to forty-five minutes, wring and dry; the bath is kept moderately warm or hot, as required by the circum-

stances. Brighter, though not fast, shades are obtained with Turkey-red oil or soap and acetate of alumina.

Wool is dyed with acetic or other acids or acid salts; the shade becomes brighter and faster to rubbing by these additions, although less intense, and the dye-bath is not thoroughly exhausted. The usual method is to dye in a hot to boiling bath with the addition of 10 to 15 per cent. sodium bisulphate. Another method, formerly in use, is the following:—Boil the wool with 5 per cent. of aluminium sulphate and 5 per cent. of acetic acid thirty minutes, then add the colour solution to this bath, dye at the boil for thirty to forty-five minutes, turning frequently, wash and dry.

A very fine brilliant blue is obtained by dyeing wool with Victoria blue in a soap-bath and subsequent stoving (like Auramine, p. 474).

Victoria blue on wool is very fast to milling, but not fast to light. It is very liable to rub owing to the superficial fixation of an insoluble blue on the fibre. This may be remedied and the shade be brightened at the same time by a subsequent soaping. Boiling with aluminium sulphate before dyeing tends also to prevent the rubbing.

Silk is dyed with Victoria blue in a bath of boiled-off liquor which has been acidulated with sulphuric acid. Add the colour solution to the warm bath, work the silk for fifteen minutes, heat to the boil, and dye until the desired shade is obtained, wash, soap (if necessary), and brighten with acetic acid; dry.

**VICTORIA PURE BLUE B (B.A.S.F.)** or **BRILLIANT VICTORIA BLUE B** (Ch. Ind. Basle) possesses the same properties as Victoria blue and is dyed in the same manner, but is distinguished by its exceedingly pure blue shade.

**VICTORIA BLUE 4 R (B.A.S.F., Ch. Ind. Basle).**

This dyestuff is *pentamethylphenyltriamidodiphenyl-naphthylcarbinol-anhydride chloride*. It is manufactured in a similar way to Victoria blue B, by the action of methylphenylalphanaphthylamine on tetramethyldiamidobenzophenone chloride. Victoria blue 4 R strongly resembles Victoria blue B in its general character and tinctorial properties, except that it dyes a redder shade. It is sold as a violet powder with a bronze reflex and dissolves in water with a blue-violet colour.

*Application.*—See *Victoria blue B*.

**NEW VICTORIA BLUE B (Bayer).** **VICTORIA BLUE R (B. A. S. F., Ch. Ind. Basle).**

This dyestuff is *ethyltetramethyltriamidodiphenyl-naphthylcarbinol-anhydride chloride*, and is obtained by the action of ethylalphanaphthylamine on tetramethyldiamidobenzophenone chloride or on tetramethyldiamidobenzohydrol.

The commercial product forms a blue or grey powder sparingly soluble in water with a blue colour; on cooling, the dyestuff separates from the solution in the shape of small green crystals. Hydrochloric acid colours the solution from green to yellow; caustic soda produces a brown precipitate. The solution in sulphuric acid is reddish-brown, and becomes, on diluting with water, yellow, green, and blue.

*Application.*—New Victoria blue is best dyed in neutral baths, both on cotton mordanted with tannin and antimony and on wool or silk, or with very small additions of acetic acid or alum or sodium bisulphate (1 to 2 per cent.). The dyed colour is more reddish in shade than Victoria blue B, but otherwise it possesses the same properties.

**NIGHT BLUE (B.A.S.F., Ch. Ind. Basle).**

Night blue is the phosphate of *tetramethyltolyltriamidodiphenyl-naphthylcarbinol-anhydride*; it is obtained by a process similar to that used for the Victoria blues (to which it is related) by the action of paratolylalphanaphthylamine on tetramethyldiamidobenzophenone chloride. It comes into the market

as a violet powder with a bronze reflex, which dissolves in water with a blue colour; the solubility is increased by acidulating with acetic acid.

Mineral acids precipitate the Night blue at first from the aqueous solution and then redissolve it with a brownish-yellow colour, diacid and triacid salts being formed. Caustic soda precipitates the colour-base as a red-brown precipitate, which is quite insoluble in water. The solution of Night blue in sulphuric acid is brown, and becomes olive-green and blue on addition of water.

Night blue is completely precipitated from the aqueous, or slightly acid, solutions by Picric acid, Naphthol-yellow, and many other dyestuffs. A method has been founded on this fact for the estimation of such dyestuffs quantitatively. (See *Analysis*, Part XI.)

*Application*.—Night blue dyes an extremely pure shade of blue, which is fast to soap on cotton, wool, and silk. The colour on silk is of extraordinary beauty. In dyeing, special care must be observed in rectifying calcareous water. The dyeing processes are identical with those given for Victoria blue B.

#### GLACIER BLUE (Ch. Ind. Basle).

Glacier blue is produced by the action of dichlorobenzaldehyde upon monomethyl *o* toluidine and oxidation of the leuco-base obtained, and is the zinc double chloride of dimethyldiamidodi *o* tolyl dichlorophenylcarbinol-anhydride.

Dark coppery powder, soluble with a fine greenish-blue colour in water acidulated with acetic acid. Hydrochloric acid (in great excess) colours the solution yellow; caustic soda produces a red precipitate. Solution in  $H_2SO_4$ , yellow; on diluting with much water, green to blue.

*Application*.—Glacier blue is dyed on cotton mordanted with tannin and antimony like the other basic dyestuffs, on wool in a slightly acid-bath, and on silk in an acidulated bath of boiled-off liquor. It yields very fine greenish-blue shades of fairly good fastness to soaping, but not fast to light. The colour is especially valuable for silk owing to its very good fastness to water on this fibre.

#### SETOGLAUCINE and SETOCYANINE (Geigy).

These two dyestuffs are produced by the action of *o* chlorobenzaldehyde on dimethylaniline or monoethyl *o* toluidine and subsequent oxidation of the resulting leuco-bases. Both are, therefore, closely related to the preceding Glacier blue.

*Setocyanine*.—Dark powder, soluble in water with a blue colour. Hydrochloric acid colours the solution brownish-yellow, while caustic soda produces a reddish-yellow precipitate. The solution in  $H_2SO_4$  is yellowish, and on diluting with water it turns at first brownish-yellow and then blue.

*Setoglaucine*.—Violet-brown powder, soluble in water with a blue colour. Hydrochloric acid colours the solution green and then yellow, finally brown; caustic soda produces a violet precipitate. The solution in  $H_2SO_4$  is yellowish-red, and on diluting with water it turns at first yellow and then blue.

*Application*.—The two dyestuffs serve for dyeing cotton and silk, especially for silk weighted with tin by the phosphate process. Silk is dyed in the acidulated boiled-off liquor. Cotton is to be mordanted with tannin and antimony. Setocyanine dyes a very fine pure neutral blue, Setoglaucine a very greenish-blue which is also very brilliant in shade. The colours are fairly fast to washing and water, but not fast to light.

#### SETOPALINE (Geigy).

Triphenylmethane colour.

Light-brown powder, not very soluble in water with a blue colour. HCl, green to yellow; NaOH, in the cold no change, on heating lighter and redder. Solution in  $H_2SO_4$ , yellow; on diluting, at first brown, then yellow.

**Application.**—Setopaline is chiefly useful for silk as it dyes a splendid blue on this fibre. It is best dissolved by boiling with some neutral soap and dyed in a neutral soap-bath or one slightly acidulated with acetic acid. Its fastness is about equal to that of the two preceding dyestuffs.

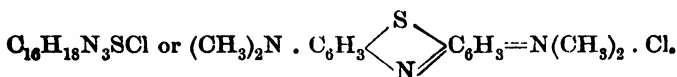
**TURQUOISE BLUE G and BB (Bayer.)**

Triphenylmethane colour.

Dark-blue powders; aqueous solution, greenish-blue; HCl, olive solutions; NaOH, brown precipitates. Solution in H<sub>2</sub>SO<sub>4</sub>, yellowish-brown; on diluting, yellowish-brown, then green, and finally blue.

These two dyestuffs are used for cotton, silk, and half-silk, and yield very fine and characteristic greenish-blue shades, the brand B B a very greenish-blue, and the brand G rather a bluish-green. The dyes are fairly fast to washing and also to water, but not fast to light. Cotton is mordanted with tannin and antimony previous to dyeing, silk is dyed in acidulated boiled-off liquor.

**METHYLENE BLUE, ETHYLENE BLUE (B.A.S.F., M.L.B., Berlin, Oehler).**



Methylene blue belongs to the group of the *thiazines* or thionine colours. It is a derivative of *thiodiphenylamine* or *thiazine*, and further of *thionine* or *paradiamidothiodiphenylamine*; the dyestuff is the chloride of *tetramethylthionine*. Methylene blue is manufactured by various methods; the process, which is most generally used, is the following:—Dimethyl *p* phenylenediamine is oxidised in the presence of sodium thiosulphate and the product of oxidation is again oxidised in the presence of dimethylaniline; the resulting product is converted by boiling with dilute acid or zinc chloride into leuco-methylene blue, and thence by further oxidation into Methylene blue.

Methylene blue forms monacid and diacid salts; the monacid salts only are stable compounds. Reducing agents convert Methylene blue into a leuco-compound from which the blue dyestuff is regenerated by oxidising agents or in contact with the air. Methylene blue occurs in commerce either as the hydrochloride or, usually, as the double salt with zinc chloride having the composition 2(C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>S<sub>2</sub>Cl) + ZnCl<sub>2</sub> + H<sub>2</sub>O. The double salt forms a dark blue or brown powder with a bronze reflex and is readily soluble in water, less in alcohol, with a greenish-blue colour; the hydrochloride forms dark blue leaflets which are readily soluble in water and in alcohol with a greenish-blue colour. Hydrochloric acid does not materially alter the aqueous solution, caustic soda makes it more violet, and, when added in a concentrated state and in excess, produces a dirty-violet precipitate. The solution in sulphuric acid is yellowish-green, and becomes blue on diluting.

**Application.**—Methylene blue possesses little value for the dyeing of wool and silk, since for these fibres other blue dyestuffs of greater brilliancy and fastness can be used. On the other hand, it is of great importance for cotton dyeing, and especially calico-printing, on account of its relative fastness both to light and to soap. It replaces for many purposes vat-indigo and is often used to brighten indigo shades. Compound shades are produced by dyeing Methylene blue with Methyl violet (see *Marine blue*), Malachite green, Safranin, and other basic dyestuffs.

Cotton is mordanted in the usual manner with tannin and antimony, and subsequently soaped as described on p. 460. For very dark indigo shades the mordanted cotton may be passed through a weak solution of pyrolignite of iron instead of being soaped; or a bath of pyrolignite of iron at 6° Tw. may be substituted for tartar emetic; after the treatment with iron liquor

the cotton should be passed through weak limewater and finally well washed before dyeing. The colour is added in small portions to the dye-bath which should not be warmer than 20° to 25° C. at the beginning, and after some colour has been taken up it should be heated very gradually to 70° or 80° or higher, if required; a small amount of acetic acid in the dye-bath acts favourably for level dyeing. The shades obtained vary from a greenish-blue—on antimony mordant—to deep indigo-blue—on iron mordant; a greater brilliancy can be imparted to them by an after-treatment in a very weak bath of stannous chloride or sodium bisulphite.

Methylene blue on cotton is distinguished by remarkable fastness to light and soap. It is much faster than most other basic colours.

A pure blue without a greenish tone can be produced with Methylene blue by means of tannate of aluminium. Mordant the cotton with aluminium acetate, age, pass through a chalk bath, wash well, pass through a weak tannin bath and dye as before. The shade is fairly fast to soap.

Wool is dyed with Methylene blue in an alkaline bath. Prepare the dye-bath with the colour solution, and with 1 to 2 per cent. (of the weight of the wool) of soda crystals or ammonium carbonate or borax; or a small quantity of ammonia may be used; enter the wool and heat slowly to boiling, boil for 30 to 45 minutes, wash and dry.

Silk is dyed in a bath containing boiled-off liquor. Add the colour-solution to the bath, enter the silk, heat to boiling and boil for twenty minutes; wash, brighten with acetic or tartaric acid, and dry.

Marine blues are mixtures of Methylene blue and Methyl violet. They are used in the same way as Methylene blue.

**THIONINE BLUE** (M.L.B., Berlin).

**TOLUIDINE BLUE** (B.A.S.F., M.L.B., Berlin).

**GENTIANINE** (Geigy).

These dyestuffs, by their chemical constitution, bear a close relation to Methylene blue, and resemble it closely in their general character and tinctorial properties.

**NEW METHYLENE BLUE N** (Cassella).

This dyestuff is also nearly related to Methylene blue and gives nearly the same reactions. It is dyed in the same manner, and closely resembles it in its general character and tinctorial properties. It dyes, however, a fuller and less greenish-blue than Methylene blue, and is preferred to the latter in calico-printing.

**NEW METHYLENE BLUE G G** (Cassella).

This dyestuff, as also New blue, Nile blue H, and BB, belong to the oxazines, and are decomposed by boiling in acid solution.\* It is an oxidised product of the condensation of New blue and dimethylaniline.

New Methylene blue G G forms a dark powder, soluble in water with a blue colour which becomes green on addition of hydrochloric acid, whereas caustic soda produces a green precipitate. The solution in sulphuric acid is brownish-red, and, on diluting with water, it becomes at first brown and then green.

*Application.*—New Methylene blue G G is dyed on cotton and silk. On cotton it is best dyed like Methylene blue or New blue, and yields a bright greenish-blue of considerable fastness to light and very good fastness to soaping. On silk it yields, in a hot acidulated bath of boiled-off liquor, a fine blue which is fairly fast to light and becomes very fast to washing by subsequent mordanting with tannin and antimony.

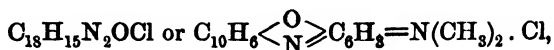
**NEW BLUE (MELDOLA'S BLUE).**

A number of blue basic dyestuffs, ranging in shade from reddish-blue to

\* J. T. Thorpe, *Journ. Soc. Dyers and Col.*, 1907, p. 164.

greenish-blue, are in the market under various names, which belong by their chemical constitution to the group of *oxazines* and are derivatives of *phenoxazine* or *anhydro-orthoxydiphenylamine*,  $C_6H_4 \langle \overset{O}{N} \rangle C_6H_4$ . They are produced by the action of nitroso-compounds of tertiary aromatic amines, or of quinone-chlorimides, or of aromatic diamines on certain phenols—*e.g.*, betanaphthol. These colours resist the action of light fairly well. (Other oxazine dyestuffs produced in a more or less different manner (Galloycyanin, Resorcin blue, &c.) belong to different classes of colours.)

The various commercial brands, such as New blue D (Cassella), Naphthylene blue R (Bayer), Fast blue for cotton (B.A.S.F., M.L.B., Berlin), Metamine blue (Leonhardt), consist chiefly of the chloride of *dimethylphenyl ammonium betanaphthoxazine*.



which is obtained by the action of nitrosodimethylaniline hydrochloride on betanaphthol. A number of other "New blues," &c., are produced by condensation of Meldola's blue with dimethyl *p* phenylene diamine, and possess essentially the same properties. We shall mention all these together under the name of "New blue," by which they are most generally known. New blues are the salts of monacid bases, and yield leuco-products by reduction, from which the dyestuffs are regenerated by the oxidising action of the atmospheric oxygen. The commercial products are either crystals or dark-violet powders with bronze reflex, the dust of which violently attacks the mucous membranes. They are readily soluble in water with a violet-blue, and in alcohol with a blue colour. Addition of hydrochloric acid makes the aqueous solution bluer, and caustic soda produces a brown flocculent precipitate. Sulphuric acid dissolves the dyestuffs with a blackish-green colour, which becomes violet to blue on diluting with water.

*Application.*—The New blues are dyed exclusively on cotton; they are not suitable for the animal fibres. It is best to dissolve the colour with the addition of some hydrochloric acid.

Cotton is mordanted with tannin (5 to 10 per cent.) and antimony in the usual way. Shades of inferior fastness are obtained by fixing the tannin in a bath of stannate of soda at  $1\frac{1}{2}^\circ$  Tw. or stannic chloride ( $3^\circ$  Tw.). Iron mordants are not recommended. The dye-bath is prepared with the necessary amount (3 per cent.) of colouring matter and 2 per cent. of hydrochloric acid (of the weight of the cotton). Enter the cotton at  $30^\circ$  and heat slowly to boiling; the bath will be exhausted. If fastness to washing is not required the tannin may be fixed in a bath of basic alum.

New blues yield indigo shades, which are fairly fast to air and light, to acids and soap. By soaping, however, they become more violet and duller; they do not resist the action of alkalies.

#### MUSCARINE (Durand).

Muscarine or *dimethylamido-oxynaphthophenazonium chloride* is prepared by the action of nitrosodimethylaniline on dioxynaphthalene (2:7). It is a salt of a monacid base, and gives on reduction a leuco-compound from which the original dyestuff is regenerated by the action of the air.

The commercial product forms a brown-violet powder, which is sparingly soluble in cold, readily in boiling water. The aqueous solution has a blue-violet colour, and gives a blue-violet precipitate on addition of hydrochloric acid; caustic soda turns it yellowish-brown. Sulphuric acid dissolves the dyestuff with a bluish-green colour; the solution becomes on dilution with water at first, blue, then violet, and finally yields a violet precipitate.

**Application.**—Muscarine is used in cotton dyeing and calico-printing, and yields reddish-blue shades of moderately good fastness. Cotton is mordanted with tannin and antimony, and in dyeing the temperature is raised to about 80°.

**NILE BLUE A (B.A.S.F., Bayer).**

Nile blue, the sulphate of *diethylamidonaphthophenoxazonium*, is formed by the action of nitrosodimethylmetaamidophenol on alphanaphthylamine. Nile blue is the monacid salt of a diacid base; the hydrochloride is very sparingly soluble in water; hence this dyestuff is sold in the form of the sulphate. Nile blue yields a leuco-compound, which is reoxidised by the air.

Nile blue occurs in commerce as a dull green crystalline powder with a bronze reflex, which dissolves sparingly in cold, readily in hot water, and in alcohol with a blue colour. From the aqueous solution the hydrochloride is precipitated on addition of hydrochloric acid in minute needle-shaped crystals, which appear violet in transmitted and green in reflected light. Caustic soda produces a flocculent dark red precipitate in the aqueous solution. Nile blue dissolves in sulphuric acid with a brownish colour which changes, through green, into blue on diluting with water.

**Application.**—Nile blue is a valuable product for the dyeing of cotton and silk, but not for wool. It yields shades similar to Ultramarine blue.

Cotton is mordanted with tannin and antimony and then soaped, as described on p. 460. Dye in a fresh bath and add the colour-solution gradually; after some of the dyestuff has been taken up heat slowly to 80° to fix the colour well, wash and dry. Beautiful light greenish-blue shades are obtained with very small amounts of dyestuff.

Nile blue on cotton equals Methylene blue in fastness to light and soap. It is very fast to chlorine, to acids, and even to alkalis (thus differing from the similarly constituted New blues).

Wool is not dyed with Nile blue, since the dyestuff fades rapidly on this fibre.

Silk is dyed at about 80° C. in neutral or acidulated boiled-off liquor.

**NILE BLUE BB (B.A.S.F.),** a similar product, yields much more greenish shades of inferior fastness to alkalis.

**CAPRI BLUE (Leonhardt).**

Capri blue, the product of the action of dimethylaniline on dimethylmeta-aminocresol, is *diethylaminotolu-dimethylaminophenoxazonium chloride*, combined as a double salt with zinc chloride.

Capri blue G O is an olive-green powder, which dissolves in water with a greenish-blue colour. Hydrochloric acid first turns the aqueous solution cobalt-blue, then blue-violet, violet, and, lastly, crimson. Dilute caustic soda has no action on the aqueous solution. The solution in strong sulphuric acid is dichroic; green in thin layers, red in thick, crimson in gas-light by transmitted light. On diluting with water a crimson solution is obtained.

**Application.**—Capri blue is dyed on cotton which has been mordanted with tannin and antimony. Enter cold, add the colour solution gradually and heat to the boil, finish boiling, wash and dry. The shade is an extremely greenish-blue, which resists light, soap, and acids well.

Silk is dyed with Capri blue with the addition of neutral soap. Enter lukewarm and bring to the boil; brighten with acetic acid. The shade is a beautiful blue-green (sea-green) in artificial light.

Similar products are **CRESYL BLUE** and **BRILLIANT CRESYL BLUE BB (Leonhardt)**, which yield very bright, but less greenish shades of blue than Capri blue.

**NEUTRAL BLUE (Cassella).**

Neutral blue, or *dimethylisocrocininduline chloride*, is related to the Safranines



by its constitution. It is produced by the action of nitrosodimethylaniline on phenylbetanaphthylamine.

Neutral blue is furnished to the trade as a brown powder, which dissolves in water and in alcohol with a violet colour. On addition of hydrochloric acid the aqueous solution becomes more bluish; caustic soda produces a violet precipitate. The dyestuff dissolves in sulphuric acid with a brown-violet colour which becomes violet on dilution with water.

*Application.*—Neutral blue is useful for the production of compound shades on cotton; it is not suited for wool and silk. Cotton is mordanted with tannin and antimony and dyed in a neutral bath at moderate temperatures. The shade is a dull blue, not fast to light or soap.

#### **BASLE BLUE R (Durand).**

Basle blue, or *toluidotolylidimethylisrosinduline chloride*, is also related to the Safranines by its chemical constitution. It is produced by the action of nitrosodimethylaniline on ditolynaphthylene diamine (2:7). A very similar Basle blue B B of a purer blue shade is produced with nitrosodimethylaniline and diphenylnaphthylene diamine.

The commercial product forms a brown-violet crystalline powder, which is soluble in water with a blue-violet colour. The aqueous solution gives a blue flocculent precipitate with hydrochloric acid, and a blue precipitate soluble in pure water with strong caustic soda. The dyestuff dissolves in sulphuric acid with an olive-brown colour which becomes green and then blue on dilution with water, and finally yields a blue precipitate.

*Application.*—Basle blue gives light reddish-blue to deep indigo-blue shades on cotton which has been mordanted with tannin; it may also be dyed with good results on wool both in alkaline and in acid baths. It serves very well for topping indigo.

*Cotton.*—For light reddish-blue shades mordant with tannin and antimony and dye with 1 to 2 per cent. of Basle blue at a moderate temperature. Then enter the dyed goods in a boiling-hot bath of sumach (20 per cent. sumach of the weight of the cotton) and soak for some hours; wring, and pass through a boiling-hot bath of antimony solution (2½ per cent. of tartar emetic); wash and dry. This after-treatment makes the shade exceedingly fast towards boiling alkalies and soap.

For the production of dark indigo-blue shades mordant with tannin (sumach) overnight and pass through a not too diluted solution of 6 per cent. copperas and ½ per cent. of chalk (of the weight of the cotton) for 15 to 30 minutes, hang some hours in the air without allowing the material to dry, wash, and dye with 2 to 4 per cent of Basle blue, hot or cold. By using more copperas and chalk (12 and 2 per cent. respectively) very dark shades are produced.

Basle blue is distinguished by relative fastness to hot soaping and to light.

*Wool.*—(1) In acid-bath prepared with 10 per cent. of Glaubersalt, 5 per cent. of sulphuric acid, and the required amount of dyestuff. (2) In alkaline bath prepare with 5 per cent. of borax and 5 per cent. of soda ash and the required amount of dyestuff. In both cases enter the wool cold and heat to the boil, boil until the bath is exhausted, wash and dry. From light to deep reddish-blue shades are obtained; those dyed in alkaline appear fuller than those in acid-baths. The colours resist boiling soap and alkalies very well.

#### **INDAZINE M (Cassella).**

Indazine M, or *dimethylphenylsafranins chloride*, is produced by heating nitrosodimethylaniline with the diphenylmetaphenylenediamine which is formed by the action of aniline on resorcin.

Indazine M is a blue powder with a bronze reflex, which dissolves in water and in alcohol with a violet-blue colour. Hydrochloric acid makes the aqueous



aniline, hydrochloric acid, and iron to 180°. Nigrosines and Indulines are found in the bye-products of the manufacture of Magenta.

The Indulines are distinguished by great fastness to light and soap.

#### INDULINE, SOLUBLE IN SPIRIT.

**FAST BLUE, COUPIER'S BLUE, AZODIPHENYL BLUE, INDIGENE, PELIKAN BLUE, INDOPHENINE B (Bayer), BLUE FOR PRINTING, ACETINE BLUE (B.A.S.F.), LEVULINE BLUE (M.L.B.), ACETINDULINE R (Cassella), NIGROSINE.**

Induline soluble in spirit is not a uniform substance; it consists of mixtures of various Indulines, chiefly of Induline  $C_{30}H_{24}N_6Cl$ , and the Indulines  $C_{36}H_{28}N_6Cl$  and  $C_{42}H_{33}N_6Cl$ . These Indulines are brought into the market in various forms. (1) As violet-black or brown-black powders, not soluble in water, but soluble in alcohol with a violet-blue colour (Induline soluble in spirit, &c.). (2) As pastes, containing substances which tend to make them soluble in water, such as aniline, hydrochloric or acetic acid (Indophenine B). (3) As a neutral blue-violet paste, which is partially soluble in water (blue for printing). (4) As solutions in levulinic or ethyl-tartaric acid or acetine, forming blue to violet-blue liquors (Levuline blue, Acetine blue, Acetinduline).

*Application.*—The Indulines serve as substitutes for vat-indigo on account of their great fastness to soap and to light. They cannot compare, however, with indigo as to beauty of shade, especially in light tints.

**Cotton.**—Induline soluble in spirit is not dyed on cotton; it can be fixed, however, on tannin and antimony mordant. Indophenine B is suitable for the dyeing of cotton by the following method:—Mordant with 3 per cent. of tannin and work for 30 to 60 minutes in a bath containing 10 per cent. of aluminium sulphate and 5 per cent. of stannate of soda (of the weight of the cotton). This bath is prepared by mixing solutions of aluminium sulphate and stannate of soda. This mordanting-bath must never react alkaline; such a reaction would indicate an excess of stannate of soda and must be corrected by adding aluminium sulphate; the bath is stirred well just before use. After mordanting, dye the cotton without washing in a fresh bath at the boil. Fuller shades are obtained by passing the dyed goods through a solution of  $\frac{1}{2}$  per cent. of potassium bichromate or nitrate of iron (of the weight of the cotton). Indophenine B yields in this way dark indigo shades, which are very fast to light, soap, and acids.

The other commercial products are valuable for calico-printing, but are not well adapted for dyeing, since they have to be fixed by steaming.

Wool is not dyed with these Indulines.

**Silk.**—Very fast shades of indigo-blue are produced on silk with Induline soluble in spirit. The dye-bath is prepared with 2 per cent. of sulphuric acid, the silk is entered at 50° and the temperature raised slowly to 80°, while the required amount of colour is gradually added.

#### PARAPHENYLENE BLUE (Dahl).

Paraphenylene blue is produced by the action of paraphenylenediamine on aminoazobenzene. Its constitution has not yet been determined with certainty. Paraphenylene blue is a monacid salt. It yields on reduction a leuco-compound, from which the original dyestuff is easily regenerated by exposure to the air. It is changed by oxidising agents, such as potassium bichromate or ferric salts, becoming darker and insoluble in water; use is made of this fact in dyeing to produce darker and faster colours.

Paraphenylene blue forms a dark violet powder, which readily dissolves in water and in alcohol with a violet-blue colour. Hydrochloric acid makes the aqueous solution bluer, caustic soda produces a violet precipitate. Sulphuric acid dissolves it with a violet-blue colour which remains unchanged on diluting with water.

*Application.*—Paraphenylene blue is especially suited for cotton dyeing, to produce deep indigo shades. It possesses extraordinary fastness to light and to soap. Cotton is mordanted in the usual way with tannin and antimony and dyed in a fresh bath; enter cold and heat to the boil. The shade can be saddened and made faster by passing the goods at 60° through a bath, containing  $\frac{1}{2}$  to 1 per cent. of bichromate of potash, after which they may be turned again a few times in the original dye-bath, washed, and dried.

#### TOLUYLENE BLUE (Oehler-Griesheim.)

This dyestuff is produced by the action of paratoluylenediamine on Induline, soluble in spirit.

Toluylene blue forms a brown-violet powder, which is soluble in water with an indigo-blue colour. A large excess of hydrochloric acid precipitates it from the solution as a polyacid salt. Caustic soda precipitates the colour-base in brown flakes. The dyestuff dissolves in sulphuric acid with a blue colour; on diluting with water a precipitate is formed which dissolves on addition of more water.

*Application.*—Toluylene blue is a good substitute for vat-indigo on cotton; and it yields shades which are distinguished by very good fastness to light, soap, acids, and alkalies.

Cotton can be dyed without a mordant or after previous mordanting with tannin and antimony. Calcareous water must be corrected with acetic acid.

(1) *Dyeing of Mordanted Cotton.*—Mordant with tannin and antimony and prepare the dye-bath with 3 per cent. of alum or 4 to 5 per cent. of acetate of chromium (25° Tw.) and with the colour-solution; enter the cotton into the cold bath, work for 20 to 30 minutes cold, heat the bath to 50° C., and work until the bath is exhausted (about 30 minutes); finally boil for 15 to 20 minutes to fix the colour better, wash, and dry. The addition of 1 to 2 per cent. of stannic salt will produce brighter shades; light indigo shades are produced by an admixture of Methylene blue. Very dark indigo shades are obtained by subsequent saddening with bichromate, which may take place in the exhausted dye-bath; add to the bath while still hot  $\frac{1}{2}$  to 2 per cent. of bichromate (of the weight of the cotton), turn for 15 to 20 minutes, and brighten by boiling the goods for 15 to 20 minutes in a soap-bath (the soap being 6 to 8 per cent. of the weight of the cotton).

(2) *Dyeing without Mordanting.*—This process is applicable for dark shades only. Prepare the dye-bath with the colour-solution (4 per cent. of Toluylene blue) and 6 to 8 per cent. of acetate of soda, and work the cotton in the unbleached state in this bath, as indicated above for mordanted goods. Subsequently, work the cotton for 15 minutes in a fresh boiling bath of 3 per cent. of bichromate and 1 per cent. of sulphuric acid or 3 per cent. of bichromate and 5 per cent. of copper sulphate, wash, and boil in 6 to 8 per cent. of soap.

#### INDAMINE BLUE (M.L.B.).

Indamine blue or *anilidophenylsafranine hydrochloride* also belongs to the soluble Indulines and closely resembles the preceding dyestuffs. It is produced by melting aminoazobenzene with a large amount of aniline hydrochloride and interrupting the melt at an early stage.

*Application and Properties.*—Same as Toluylene blue.

#### METHYLINDONE (Cassella).

This dyestuff also belongs to the soluble Indulines and is sold as Methylindone B and R.

*Application.*—Methylindone is dyed on cotton mordanted with tannin and antimony; it yields very bright indigo-blue shades which are superior to vat-indigo in fastness to light and exceedingly fast to soap, alkalies, and acids.

**INDOÏNE BLUE** (B.A.S.F., Geigy), **DIAZINE BLUE** (Kalle), **NAPHT-INDONE** (Cassella), **INDOL BLUE** (Berlin, Leonhardt), **FAST COTTON BLUE R** (Oehler-Griesheim), **JANUS BLUE** (M.L.B.), **VACANCEÏNE BLUE** (Holliday), **MADRAS BLUE** (Poirrier).

Basic dyestuffs of indigo blue shades and of exceedingly good fastness to soap and light are produced according to various patents by the action of diazotised Safranine on beta-naphthol. These dyestuffs are also distinguished by the property of dyeing fairly fast shades on unmordanted cotton.

The products are furnished in the form of various brands (*e.g.*, BB, BR, R, G, RG, &c.) slightly differing in shade. They form dark-brown or blackish powders or pastes which readily dissolve in pure water or water slightly acidulated with acetic or other acids, but are precipitated by alkaline water. The aqueous solution is reddish-blue or violet. Hydrochloric acid produces a soluble dark-blue precipitate; caustic soda completely throws down the colour-base in the form of a black precipitate. The solution in sulphuric acid is olive-green to blackish-green, and on diluting it becomes at first green, then blue and violet. (The dyestuffs are easily converted into Safranine and then decolourised by reduction with zinc and hydrochloric acid, or with titanous chloride; on re-oxidation they furnish the red colour of Safranine, not the original blue colour.)

*Application.*—The dyestuffs are used almost exclusively for dyeing fairly dark shades on cotton and silk. In calico-printing use has been made of the property of converting the blue into red by reduction and re-oxidation, in order to produce red patterns on a blue bottom. A similar effect may be obtained by printing on alkalis or alkaline salts and steaming.

The dyestuffs are best dissolved by mixing them with their own weight of acetic acid and boiling with hot water for a short time.

Cotton is mordanted in the usual way with tannin and antimony. For light and medium indigo shades, 7 to 13 per cent. sumach and  $\frac{3}{4}$  to  $1\frac{1}{2}$  per cent. antimony salt; for dark shades, 13 to 20 per cent. sumach and  $1\frac{1}{4}$  to 2 per cent. antimony salt are most suitable. Careful dyeing is necessary in order to produce even shades. Prepare the dye-bath with 2 to 4 per cent. alum or aluminium sulphate and use only a part of the dyestuff (which should be carefully dissolved). Enter cold, or at most at a hand-warm temperature, and add the rest of the dyestuff very gradually after the first portion has been fairly exhausted; finally boil fifteen to forty-five minutes. The use of calcareous water increases the depth of shade, but is detrimental to levelling, and is, therefore, to be recommended only for deep shades. Alum and aluminium sulphate act both as general levelling agents and especially as preventives of the formation of spots caused by separation of the free colour-base. Two per cent. of dyestuff yields a full blue and 3 per cent. a very dark blue, which closely resembles vat-blue shades. In order to make the colour more coppery it is useful to add to the exhausted bath 4 to 6 grms. calcium acetate per kilo. cotton (6 to 10 ozs. per lb.); the colour becomes less reddish by boiling one-half hour longer in the dye-liquor or, better still, in the mordanting liquor which has been freshened up with some sumach.

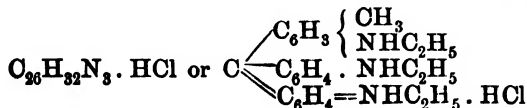
The fastness to light, washing, alkalis, and acids is exceedingly good; the dyestuffs belong to the fastest basic colours and to the best substitutes of vat blue, which they almost reach or practically equal in fastness. They fade very slowly on exposure to air, thereby becoming reddish-grey, and by alkaline washing they suffer somewhat more than indigo, but withstand ordinary soaping exceedingly well.

When dyed direct without previous mordanting they are also relatively fast, but not so fast as on a mordant of tannin and antimony. Prepare the bath with 2 per cent. alum of the weight of the goods and add the well

dissolved dyestuff gradually, enter cold or lukewarm, and after the bath is fairly exhausted, boil one-quarter to one-half hour. The method indicated on p. 462 may also be used with advantage, the fastness of the colours obtained lying between those of the direct shades and those dyed on previously mordanted cotton.

Silk is dyed in acidulated boiled-off liquor and the colour obtained is very fast to light, water, and washing. Unions and satins, see p. 464.

**METHYL VIOLET R to 5 R, HOFMANN'S VIOLET, PRIMULA, DAHLIA.**



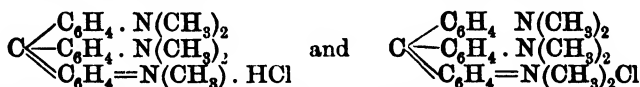
Hofmann's violet consists of various methyl- and ethyl-derivatives of Magenta, which were originally produced by methylating or ethylating Magenta with methyl or ethyl iodide, one, two, or three methyl or ethyl groups combining with the rosaniline base. The hydro-iodides thus formed were converted into the hydrochlorides, which are more freely soluble in water. The ethyl-derivatives dye a redder shade than those of methyl. The violets form salts, with one, two, and three equivalents of acids; the monacid salts only are stable in solutions. They yield leuco-compounds, from which the original dyestuffs are regenerated by the action of oxidising agents.

Violet 5 R, the reddest of the violets, shows the following reactions:—It is a green crystalline powder, soluble in water, with a magenta-red colour. The aqueous solution is turned yellowish-brown by hydrochloric acid, and gives a brown precipitate with caustic soda. Sulphuric acid gives a yellowish-brown solution which remains unchanged on diluting with water.

*Application.*—Hofmann's violet has been almost completely replaced by ordinary Methyl violet, and is used nowadays for white dyeing of wool only. It yields very pure red-violet shades, the reddest of the various Methyl violets. For methods of dyeing, see p. 494.

**METHYL VIOLET B and 2 B. PARIS VIOLET.**

The ordinary Methyl violets are mixtures of the hydrochlorides of various methylated pararosanilines, and consist chiefly of the two salts



*Pentamethyl pararosanine hydrochloride. Hexamethyl pararosanine chloride.*

Methyl violet is produced by the oxidation of dimethylaniline with cupric chloride. The more methyl groups there are in the product, the bluer is the shade. In its general chemical character Methyl violet resembles Hofmann's violet. The commercial product is the hydrochloride, which occurs as a powder or in irregular lumps having a green metallic reflex. It dissolves in water and in alcohol, as also in amyl-alcohol, with a violet colour. On addition of hydrochloric acid, the solution becomes yellowish-brown; caustic soda gives a brown-red precipitate. Sulphuric acid dissolves the dyestuff with a yellow colour, which becomes, on diluting with water, at first yellowish-green, then greenish-blue, and, finally, violet.

*Application.*—See next page.

Methyl violet is also used as an antiseptic, and is brought into the market for this purpose in a pure state, under the name "*Pyoktanin coeruleum*," by E. Merck (Darmstadt).

**METHYL VIOLET 6 B or BENZYL VIOLET.**

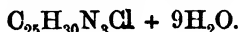
Methyl violet 6 B or *pentamethylbenzylpararosanine chloride* is a benzylated

Methyl violet produced by the action of benzyl chloride on ordinary Methyl violet. Methyl violet 6 B is very similar in its reactions and properties to Methyl violet B and 2 B.

*Application.*—See below.

Methyl violet 3 B, 4 B, and 5 B are mixtures of the ordinary Methyl violet and Methyl violet 6 B. Methyl violet 7 B and *Marine blue* (see p. 485) are mixtures of Methyl violets and Methylene blue. Mixtures of Methyl violets with Malachite green are met with in commerce under the names of *Fast blue*, *Indigo blue*, &c., and mixtures with Magenta are offered as *Dahlia* and *Primula*.

**CRYSTAL VIOLET** (B.A.S.F., Ch. Ind. Basle, Sandoz, &c.).



Crystal violet is *pure hexaethylpararosniline chloride* produced by the action of phosgene gas on dimethylaniline. It is brought into commerce in well-defined crystals, which contain eight equivalents of water of crystallisation, and possess a peculiar greenish-brown metallic reflex, or as a greenish powder. It dissolves very easily in water and in alcohol, with a deep violet-blue colour. Hydrochloric acid turns the aqueous solution first blue, then green, and finally yellow, with formation of polyacid salts; caustic soda produces a violet precipitate. Sulphuric acid dissolves the dyestuff with a yellow colour, which passes, on dilution with water, through olive-green and blue into violet. Crystal violet belongs to the Methyl violets, but possesses the advantage of great colouring power, extreme solubility, and of having no tendency to produce a bronze scum on the dye liquor or on the goods. It dyes a very bluish-violet of great purity.

*Application.*—See below.

**ETHYL PURPLE** or **VIOLET 6 B** (B.A.S.F., Ch. Ind. Basle).

This dyestuff consists of *pure hexaethylpararosniline chloride*. It is analogous in constitution to Crystal violet, and is similarly prepared by the action of phosgene gas on diethylaniline. The commercial product forms a green crystalline powder, which is easily soluble in water, with a violet-blue colour, and resembles Crystal violet in its reactions and properties. It dyes the bluest violet shade of the various Methyl violets—still bluer than Crystal violet, and equal in purity to the latter.

*Applications of the Methyl Violets.*—The various Methyl violets are very similar in their properties; they are readily soluble in water and dye from reddish- to bluish-violet shades on the vegetable and animal fibres. They are frequently used to brighten other colours by topping—*e.g.*, vat-indigo, logwood, Alizarine violet, Direct cotton colours and Sulphide colours.

The Methyl violets are not fast to light.

Cotton is mordanted with tannin and antimony and dyed in a fresh lukewarm bath as usual for Magenta, &c. The shade is fairly fast to soaping. Dark shades are obtained by fixing the tannin with iron solutions, to which aluminium sulphate may be added for shading. The fixing-bath can be dispensed with if fastness to washing is not required. In the latter case the two following methods, which give brighter shades, may be used:—Work the cotton for half an hour in a bath containing 10 per cent. of its weight of alum, wring without washing, and work it for 20 minutes at 50° to 60° in a bath containing 5 per cent. of its weight of soda crystals; rinse the cotton well and dye in a fresh lukewarm bath; wring and dry without washing. Or prepare for 10 kgs. (lbs.) of cotton a mordanting-bath as follows:—50 grms. ( $\frac{3}{4}$  oz.) each of acetate of lead and tin crystals are dissolved together in 200 litres (20 galls.) of hot water; the mixture is allowed to stand until the precipitate formed has settled; then the clear liquor is run off and used. Enter the cotton into the clear liquor, heat to 70° or 80° C., turn for half an hour, and then pass into a





**Perkin's Violet, Rosolane, Mauveine, Chrome Violet, &c.**

This compound possesses great historical interest, since it was the first aniline dyestuff introduced into commerce, and was the immediate cause of the grand development of the aniline industry. It was discovered in 1856 by W. H. Perkin, and was subsequently manufactured and introduced by him as Tyrian Purple. The formation of the dyestuff was observed as early as 1834 by Professor Runge of Berlin; at that time, however, coal-tar and aniline had not received the attention that was given to them twenty years later, so that Runge was unable to convince capitalists of the importance of his discovery, and, owing to lack of funds, did not succeed in introducing it into practical use.

Perkin obtained the dyestuff, Mauve, by oxidising aniline oil containing toluidine with chromic acid, and by this method it is still manufactured. Mauve belongs to the Safranines and is a mixture of salts of *phenyl-* and *tolyl-safranines*.

The commercial product is the hydrochloride or sulphate. It occurs as a red-violet paste; or, in crystals, which are sparingly soluble in cold, more freely in hot or acidulated water, with a violet-red colour. Hydrochloric acid does not alter the aqueous solution; caustic soda produces a violet-blue precipitate. Sulphuric acid dissolves the dyestuff with an olive-green colour; the solution becomes, on dilution with water, at first blue and then violet-red.

Ethylated Mauve has been brought into commerce under the name of *Dahlia*, which closely resembles Mauve.

*Application.*—Mauve dyes a dull violet of the shade of the old British penny stamps, which were printed with mauve. In the production of bright greys it is used as a substitute for orchil and ammoniacal cochineal.

Mauve is much faster to light than the Methyl violets and equally fast to washing; it is applied in the same way as they are, to the various fibres. It may also be dyed on unmordanted cotton.

**RÓSOLANE (M.L.B.), TANNIN HELIOTROPE (Cassella), GIROFLÉ (Durand), METHYLENE VIOLET (M.L.B., Durand), CLEMATINE (Geigy), FUCHSIA (Oh. Ind. Basle), RUBRAMINE (Noetzel), SAFRANINE M N (B.A.S.F.).**

These dyestuffs belong to the Safranines and are identical with or very similar to each other. They are produced by oxidising amidodimethylaniline, together with the toluidines, or by the action of nitrosodimethylaniline on toluidine or xylidine or by similar reactions. The commercial products form brown or glistening green powders, which show reactions similar to those of the Safranines. They are applied exactly like the Safranines and are useful dyestuffs, especially for cotton dyeing and calico-printing. Their red-violet shades are not quite equal in beauty to those of the Methyl violets, but very much faster to light and very good to washing.

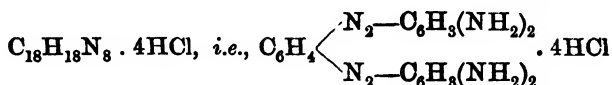
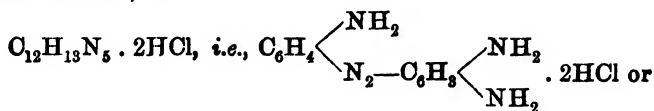
**PARAPHENYLENE VIOLET (Dahl).**

This product is an amino derivative of *phenylrosinduline*, and is formed by fusing paraphenylenediamine with azo-compounds of alphanaphthylamine in the presence of benzoic acid. It forms a dark brown powder, soluble in water with a violet colour. Hydrochloric acid causes no changes, while caustic soda produces a violet precipitate. The solution in sulphuric acid is blue-violet and becomes less bluish on diluting.

*Application.*—Paraphenylene violet is used in cotton dyeing and printing, and is applied in precisely the same way as Paraphenylene blue (see p. 490). It is distinguished by superior fastness, but it does not equal the blue in this respect.

**BISMARCK BROWN.**

**MANCHESTER BROWN, PHENYLENE BROWN, VESUVINE, CANELLE LEATHER BROWN, &c.**



Bismarck brown is produced by the action of nitrous acid on meta-phenylenediamine, and its constitution probably corresponds to one of the above formulæ (or to both).

Similar products are obtained by diazotising toluylenediamine; they dye redder shades of brown. Bismarck brown is a diacid (or tetracid) salt, which is converted by reducing agents into phenylenediamine and triamidobenzene, not into a leuco-compound.

The commercial product is a dark brown powder, soluble in water, with a brownish colour. Hydrochloric acid makes the solution more yellowish, and caustic soda produces a brownish flocculent precipitate. Sulphuric acid dissolves the dyestuff with a brown colour, which is turned brownish-yellow on dilution with water.

*Application.*—Bismarck brown resembles Chrysoïdine (see p. 471), both chemically and in its application. It dyes a bright shade of brown, similar to, but redder than, catechu. The dyestuff has been employed to a great extent on the various fibres, and is still used in great quantities. It has, however, lost much of its former importance, as it is not fast to light, soap, or milling. It is largely used in the dyeing of leather.

Bismarck brown should be dissolved in water free from lime at about 80° C. The solution must not be kept for a long time, since it gradually decomposes spontaneously.

*Cotton.*—Bismarck brown is applied in the same way as Chrysoïdine. It can also be fixed on tannin and iron. The shade becomes redder if alum is added to the dye-bath. Catechu is brightened by topping with Bismarck brown. The dyestuff is useful for the production of compound shades in combination with the other basic colours and for brightening the direct cotton colours, sulphide and wood colours.

Wool may be dyed with Bismarck brown as with Chrysoïdine.

Silk is dyed by the same method as is described under *Chrysoïdine*.

**METHYLENE GREY (M.L.B.), NEW GREY (Bayer), NIGRISINE, MALTA GREY (Poirrier), FAST GREY (Oehler-Griesheim).**

The composition and constitution of this dyestuff are not yet known. It is produced by boiling the aqueous or alcoholic solutions of nitrosodimethylaniline hydrochloride or by the oxidation of para-amidodimethylaniline.

It forms a greyish-black powder, which dissolves in water with a reddish-grey colour. Hydrochloric acid makes the solution bluish-grey. Caustic soda produces a dark grey precipitate. Sulphuric acid dissolves it with a greyish-yellow colour which becomes reddish-grey on dilution with water.

*Application.\**—This grey is sometimes used for the dyeing of cotton and of cotton and silk mixed goods, and in calico-printing. It dyes a pure grey, and is relatively fast to light and soap. Calcareous water is corrected with hydrochloric acid.

\* Th. Baumann, *Journ. Soc. Dyers and Col.*, 1890, p. 96.

Cotton is mordanted with tannin and antimony and dyed in a neutral bath, the temperature of which is gradually raised during one hour to the boil.

The dyestuff can also be dyed without a mordant on cotton, even in the presence of hydrochloric acid. In this case it is steamed or aged after dyeing and then passed through a bichromate bath ( $\frac{1}{2}$  per cent. solution) at 60°. The shade is more reddish than on tannin mordant. The addition of acetic acid to the dye-bath makes it bluer.

Silk and cotton and silk mixed goods are dyed in a neutral bath without mordants.

#### **NIGROSINE (SOLUBLE IN SPIRIT). SILVER GREY, STEEL GREY.**

Nigrosine is a product similar to Induline. It is not a homogeneous substance and its composition is not known. It is prepared by melting a mixture of nitrophenol with aniline and aniline hydrochloride in the presence of iron.

The Nigrosine of commerce is a greyish-black powder soluble in alcohol but not in water. It resembles Induline.

*Application.*—Nigrosine dyes fast shades of bluish-grey. It is not used much in dyeing, since it yields light shades only; but it is used to some extent in printing cotton and silk piece goods and for colouring varnishes, spirit varnishes, oils, fats, and waxes. It is applied to the various fibres in the same way as Induline, soluble in spirit.

#### **FAST BLACK (Leonhardt).**

Fast black is the product of the reaction of nitrosodimethylaniline with metaoxydiphenylamine. It forms a black powder, which is soluble in water with a violet-black colour; the aqueous solution gives a black precipitate on addition of hydrochloric acid, while caustic soda produces a violet-black precipitate. The solution in sulphuric acid is almost black, and becomes violet-black on diluting with water.

*Application.*—Fast black is dyed on cotton mordanted with tannin and antimony. It produces a blue-black shade, which is fairly fast to light, soap, acids, and alkalis. A deep black of very good fastness is obtained on a mordant of sumach and iron.

#### **DIAZINE BLACK (Kalle).**

Azo-colouring matter, produced by the action of diazotised Safranine on phenol, analogously to Diazine blue and Diazine green.

Diazine black forms a dark brown powder which dissolves in water with a blackish green-blue colour and in alcohol with a reddish-blue colour. Hydrochloric acid produces in the aqueous solution a soluble black-green precipitate, caustic soda a red precipitate. The solution in sulphuric acid is green, and on diluting it becomes at first violet and then yields a black-green precipitate. Diazine black is decolourised by reduction with zinc and acid; the solution becomes pink in the air by formation of Safranine.

*Application.*—Diazine black is dyed, like Diazine blue, on cotton either mordanted with tannin and antimony or non-mordanted; an addition of some alum is useful for levelling. It yields on mordanted cotton with 4 per cent. of dyestuff a black of very good fastness to soap and light.

**JANUS BLACK (M.L.B.)** is a dyestuff similar to Diazine black, and applied in the same manner (see also pp. 462 and 464).

## **EOSINS AND RHODAMINES.**

The dyestuffs which are described in this chapter are closely related to each other by their chemical constitution. They dye shades ranging from yellow to bluish-red, which are distinguished by an extraordinary brilliancy.

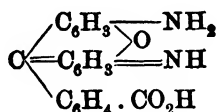
All the Eosins are derivatives of Fluorescein, which is produced by the condensation of phthalic anhydride,  $C_6H_4 \langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \rangle O$ , and resorcin:—



Fluorescein is a derivative of triphenylmethane carboxylic acid. (Structural formula, see on p. 502.)

The various commercial Eosins are the alkali salts of chlorine-, bromine-, iodine-, or nitro-substitution derivatives of Fluorescein or the methyl- and ethyl-ethers of Fluorescein and some of its derivatives; Chrysolin is a benzylated Fluorescein, and Cyclamin is a sulphur derivative.

Rhodamine B is obtained like Fluorescein by the condensation of phthalic anhydride with diethylmetamidophenol. Its parent substance is Rhodamine or diaminophenolphthalein.



Most of the other Rhodamines are derivatives of this substance.

Rhodamine S resembles the other Rhodamines constitutionally; it is not produced, however, from phthalic anhydride, and does not belong to the triphenylmethane group. It is formed by the condensation of succinic anhydride,  $C_2H_4 \langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \rangle O$ , with diethylamidophenol, and is a derivative of diphenylmethane (the constitutional formula is given on p. 508, Rhodamine S). The commercial Rhodamines are the basic (*i.e.*, monacid) hydrochlorides of organic bases. Rhodamine S is the zinc chloride double salt.

Rhodamine B, the oldest member of this group, forms, so to say, the connection between the basic and the acid dyestuffs, as it possesses both basic and acid characters, and may be dyed both on tanned cotton and in an acid bath on wool or silk. Some of the Rhodamines, the so-called Anisolines, Irisamine, and the Rhodines have no acid character, their acid group, the carboxylic group, being etherified. The Eosins, on the other hand, have the property of feeble acids.

To the group of the Rhodamines also belong the acid Violamines (*see Acid Colours*).

All the compounds of this group are converted into leuco-compounds by reduction, and are regenerated more or less rapidly by oxidation; but the original dyestuffs are not always reproduced, since the substituting groups—such as bromine or iodine—are frequently eliminated by the reducing agents.

The colours are mostly soluble in water and in dilute alcohol; those which are sparingly soluble in water are dissolved in alcohol before use—*Spirit-Eosins*. The solutions show more or less intense fluorescence, which is stronger in alcoholic solutions (the Erythrosins do not fluoresce in aqueous solutions, and Eosin B N very little).

The colours of this group dissolve in concentrated sulphuric acid with a yellow colour, while they vary in their reactions towards hydrochloric acid and caustic soda according to their phenolic or basic character. Fluorescein and its derivatives remain in solution on addition of caustic soda, and are precipitated by hydrochloric acid; the reverse reactions take place with the Rhodamines. Chloride of lime decolourises the solutions on heating. The Eosins form lakes with various metallic salts, especially with lead salts; some of these are ex-

tensively used on account of their great brilliancy as pigments (vermillionettes). Most of the Eosins may be recognised by the fluorescence of their solutions, especially in the presence of ammonia; those which do not fluoresce yield, when reduced and re-oxidised, the intensely fluorescent Fluorescein, and they can be detected in this way. The Rhodamines fluoresce in aqueous solutions at the ordinary temperature but not at the boil. The Eosins and Rhodamines are distinguished by their phenolic or basic characters respectively, especially on shaking with ether. If the bromine or iodine derivatives of Fluorescein are dissolved in strong sulphuric acid and the solution is heated, bromine or iodine escapes; the former is detected by the smell, the latter by reacting on moist starch paper and by evolving violet vapours.

The Eosins which are freely soluble in water are stripped from the fibres by dilute alkalies, the Spirit-Eosins by alcohol; the Rhodamines are extracted to some extent both by alkalies and by alcohol. The dyestuffs can be recognised by their fluorescence, &c., in the solutions thus obtained. Care should be taken, however, not to confound them with Thioindigo red.

The quality and strength of the Eosins and Rhodamines are estimated by dye-tests. The strength may also be determined by titration with  $TiCl_3$  (see Part IX.). The Eosins are dyed, with the addition of common salt, both on wool and on unmordanted cotton—as described below; the Rhodamines are tested on wool or silk.

*Application of the Eosins and Rhodamines.*—The Eosins and Rhodamines can be dyed both on the vegetable and on the animal fibres. The Eosins have been valued very highly for the brilliancy of their shades, which is surpassed by no other group of colours. They are still used for this reason in silk dyeing, especially the Spirit-Eosins, which give brighter colours than the soluble Eosins, and are distinguished by a very intense fluorescence. In the dyeing of wool and cotton, however, they have been replaced to a great extent by other dyestuffs, which are both less fugitive and less expensive, frequently the property of fluorescing is objectionable. Indeed, the Eosins are rarely dyed on wool, and to a limited extent only on cotton, since the azo-dyestuffs have come into the market. The before-mentioned lakes (vermillionettes) are still largely employed as steam colours in calico-printing (especially to produce reds on indigo blue). These lakes are used, however, in much larger quantities for the colouring of paper and for painting; they are of great value for these purposes, not only on account of their extraordinary brightness, which rivals that of genuine vermilion, but also for their being comparatively fast to light (in contrast with the Eosins which are dyed on the textile fibres).

The Rhodamines are not inferior to the Eosins in beauty and brilliancy of shade, and they evince also strong fluorescence on the animal fibres. The Rhodamines of acid character (B, G, 3 B) are not of great value for the dyeing of cotton, since they cannot be fixed on this fibre permanently without losing their brilliancy; they possess, however, considerable fastness both to light and to soap on silk and wool, and they are used with advantage to produce brilliant red shades on these fibres. The Rhodamines which possess merely basic character, like the various Anisoles, Rhodines, and Irisamine, are, however, of great value for the production of brilliant pink and red shades, fast to washing on tanned cotton. Rhodamine S is recommended for the dyeing of non-mordanted cotton, and of cotton and silk mixed goods.

The Eosins soluble in water require about 30 parts of hot water for solution. Since they form insoluble lakes in hard water, soft water or water which has been boiled with sodium carbonate should be used; the latter may be employed in its weakly alkaline state. The Eosins, soluble in spirit, are dissolved in diluted methylated spirits, as described on p. 459. The Rhodamines are dissolved, like the basic colours, in about 250 parts of hot water.

*Application on Cotton and Linen.*—The *Rhodamines*, with the exception of Rhodamine S, are usually dyed on tannin-mordanted cotton like the basic colours, as will be indicated with the special description of the several brands.

The *Eosins* are dyed by the following methods:—

*First Method.*—The dye-bath is prepared with a lukewarm solution of common salt to stand at 6° Tw.; the colour solution is added and the material turned in the liquor at 40° to 50° for forty-five minutes, then wrung, and dried without washing. The bath should be very concentrated (amounting to not more than ten times the weight of the cotton), and is kept for further use. Light shades only can be produced, and the colour is stripped by rinsing with water.

*Second Method.*—The material is first worked in a lukewarm bath of sodium stannate, and, after steeping for two to three hours, treated for about the same time in a bath of basic alum. After this it is wrung, dyed as by the first method, and dried without washing. All the liquors should be very concentrated; the dye-bath is not exhausted. The shade is not fast to soap, but faster to rinsing with water and more intense than that obtained by the first method. Use, for 10 kgs. (10 lbs.) cotton,

½ kg. (½ lb.) of stannate of soda,  
 ½ kg. (½ lb.) of alum, and  
 100 grms. (1½ oz.) of soda crystals;

dissolve the alum and the soda crystals separately, and mix the solutions.

*Third Method.*—The goods are saturated with a solution of Turkey-red oil—50 grms. per litre (½ lb. per gall.)—wrung, dried or steamed, turned for half an hour in acetate of alumina (3° Tw.), dried, passed through a weak chalk bath, and well washed in water. After this the material is dyed as by the first method. A hot strong solution of soap may be used with similar results instead of the Turkey-red oil. The dye-bath is not exhausted, and the shades resemble, both in appearance and in fastness, those obtained by the second method. The following method of mordanting, which is recommended by the Badische Anilin- und Soda-Fabrik, allows of obtaining uniform shades through the material:—Prepare a stock liquor of 1 part Turkey-red oil and 2 parts water, and put 12 to 15 litres (2½ to 3¼ galls.) into a tramping dish. Mordant one handful (i.e., 2 lbs.) of bleached dry yarn in this liquor, wring well, mordant again, wring and level at the wringing-post, strike out, and dry. For freshening up the bath, use, for each handful of yarn, 1 litre (1 quart) of liquor prepared by diluting 3 parts of stock liquor with 1 part water, and treat the whole lot in the same way. Dry at a moderate temperature. Repeat the whole treatment once or twice, diluting the stock liquor so that the bath always remains of the same strength.

In order to test the strength of the mordanting bath during working, shake 50 c.c. of the liquor, before beginning to work and from time to time during the working, with 10 c.c. sulphuric acid in a graduated 100 c.c. cylinder, allow the oil to separate, and read off the number of c.c. of oil. The quantity of oil which separates should always remain the same.

*Fourth Method.*—More bluish shades are produced with the *Eosins* if, in the third method, a solution of a basic lead salt (at about 3° Tw.) is substituted for the red liquor. The goods may also be impregnated first with the lead salt, passed through ammonia, washed in water, and then dyed. The use of lead salts has the disadvantage that the colour is blackened by sulphuretted hydrogen.

*Application to Jute.*—Jute is dyed at the boil, with the addition of some alum and acetic acid, washed, and dried.

*Application to Wool.*—Wool is dyed with the *Eosins* at the boil with

the addition of acetic acid or alum. Alum gives the brighter shades, but the wool has a harsher feel than when dyed with the addition of acetic acid. Boil for 20 minutes, wash and dry. Better results are obtained by the following method:—Prepare the bath for 10 kgs. (10 lbs.) wool with

200 litres (20 galls.) of water,  
 $\frac{1}{2}$  kg. ( $\frac{1}{2}$  lb.) of alum,  
 300 grms. (5 ozs.) of tartar, and  
 $\frac{1}{2}$  kg. ( $\frac{1}{2}$  lb.) of acetic acid;

work the wool for half an hour in this bath at the boil, allow to cool, add the colour solution, turn quickly for 15 minutes, heat gradually to boiling, turn for 15 minutes more, wash, and dry. The bath is exhausted, if it is sufficiently acid; otherwise more acetic acid may be added.

The *Rhodamines* may be dyed like the Eosins. They are, however, best dyed in a feebly acid bath:—Prepare the bath for 10 kgs. (10 lbs.) wool with

1 to 2 kgs. (lbs.) Glaubersalt,  
 200 to 500 grms. (3 to 8 ozs.) acetic acid,

and the requisite quantity of dyestuff; enter at 40°, heat to the boil, and boil for one-half to three-quarters of an hour. Instead of acetic acid 200 to 400 grms. (3 to 6 ozs.), sulphuric acid may be used or the dyeing may be carried out without the addition of any acid in a neutral bath. Dyeing in a neutral bath is especially useful in the one-dip method of union dyeing with direct cotton colours (see p. 386) in order to shade the wool.

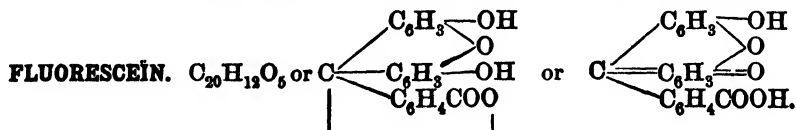
The Eosins are very fugitive to light; the Rhodamines are much faster in this respect. Both groups of colours are fairly fast to milling, and fast to acids, alkalis, and stoving.

*Application to Silk.*—Silk is dyed with the Eosins with the addition of acetic acid or in a bath of boiled-off liquor which has been acidulated with tartaric or acetic acid. Use for 10 kgs. (10 lbs.) of silk

30 litres (3 galls.) of boiled-off liquor,  
 270 litres (27 galls.) of water,

and sufficient acid to make the bath slightly acid; add the colour solution, turn the silk while heating to the boil, and work for half an hour in the boiling bath; wash, and brighten in a warm bath containing a little acetic or tartaric acid, wring, and dry.

The *Rhodamines* are best dyed in a neutral bath of boiled-off liquor or in one slightly acidulated so as to just give a sour taste. Enter the silk at 40° C., turn a few times, add the colour solution, turn rapidly six times, heat to 60° C. and finally to boiling. Or the silk is dyed without boiled-off liquor. Enter at 60° C., heat to 80° C., and add sufficient acetic acid to exhaust the bath.



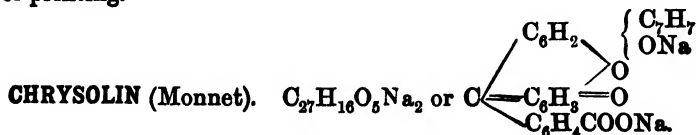
Fluorescein, the mother-substance of the Eosins, is produced by heating 1 molecule of phthalic anhydride and 2 molecules of resorcin to 200° C. in the presence of zinc chloride. It forms a dark yellow crystalline powder, which is very sparingly soluble in the usual solvents, except dilute alkalis and hot glacial acetic acid. It possesses little tinctorial power and is not a commercial article.

URANIN ( $C_{20}H_{10}O_5Na_2$ ). FLUORESCEIN.

Uranin is the sodium salt of Fluorescein. Yellowish-brown powder;

aqueous solution, yellow with intense green fluorescence; HCl, yellow flocculent precipitate; NaOH, darker with a dark green fluorescence; solution in H<sub>2</sub>SO<sub>4</sub>, yellow; on diluting with water, yellow.

Uranin dyes wool and silk yellow, and is used to a very limited extent in wool printing.



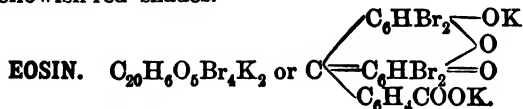
Chrysolin, the sodium salt of a benzylate fluorescein, is produced by heating phthalic anhydride, resorcin, and benzyl chloride together in the presence of sulphuric acid.

Reddish-brown powder or lumps with a greenish reflex; aqueous solution, brown with a green fluorescence; HCl, brown-yellow precipitate; NaOH, darker; solution in H<sub>2</sub>SO<sub>4</sub>, yellow; on diluting, yellow precipitate.

Chrysolin dyes a yellow shade which is very similar to turmeric; the colour is moderately fast to light on the animal fibres. It is used sometimes in cotton dyeing for topping quercitron yellow.

**AUREOSIN**, a chlorinated fluorescein, and **RUBEOSIN**, a nitrated aureosin, have disappeared from the market.

**EOSIN ORANGE** and **EOSIN 3 G** are mixtures of dibrom- and tetrabromfluorescein, which behave similarly to Eosin, and yield orange and yellowish-red shades.



**EOSIN, YELLOWISH; EOSIN, SOLUBLE; EOSIN G, J, A, B, G G F, &c.**

Eosin is the potassium- (or sodium-) salt of tetrabromfluorescein, and is produced by the action of bromine on fluorescein.

Eosin comes into the market in the form of small red crystals with a bluish reflex, or as a dark red amorphous powder, and is completely soluble in three times its weight of water, with a red colour; the dilute aqueous solution is pink coloured with an intense yellowish-green fluorescence. The alcoholic solution evinces a still more intense fluorescence. Mineral acids precipitate from the aqueous solution of Eosin tetrabromfluorescein in the free state as an amorphous orange-coloured powder, which is nearly insoluble in water; it dissolves in alcohol with a reddish-yellow colour without showing fluorescence. Tetrabromfluorescein is a fairly strong acid, and its salts are not decomposed by acetic acid. The aqueous solution of Eosin becomes darker on addition of caustic soda, and produces a soluble yellowish-red precipitate. The solution in strong sulphuric acid is yellow, and yields, on diluting with water, a yellow flocculent precipitate.

Eosin dyes a more yellowish shade than any of the following Eosins or Rhodamines. The colour is a yellowish-pink, or, in conjunction with lead mordants, a cherry-red.

**ERYTHRIN**. C<sub>20</sub>H<sub>6</sub>Br<sub>4</sub>O<sub>6</sub>(OCH<sub>3</sub>)(OK).

**EOSIN, SOLUBLE IN SPIRIT; PRIMEROSE À L'ALCOOL; METHYL-EOSIN.**

Erythrin is the methyl-ether of Eosin, and is produced by heating Eosin with wood spirit and sulphuric acid.

Dark red powder with a green reflex, sparingly soluble in water, not



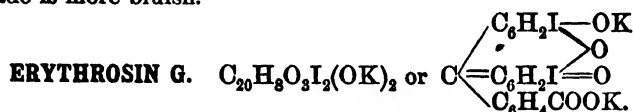
soluble in absolute alcohol, but freely soluble in alcohol containing 50 per cent. water. This solution is red with a brownish-yellow fluorescence. HCl produces in the aqueous solution a brown-yellow precipitate; NaOH makes the aqueous solution darker; solution in  $H_2SO_4$ , yellow; on addition of water, brown-yellow precipitate.

Erythrin dyes a pink shade with a brick-red fluorescence, which is more bluish and brilliant than Eosin. The colouring matter is added to the dye-bath in alcoholic solution. Its application is restricted to the dyeing of silk and to the colouring of spirit varnishes.

**PRIMROSE.**  $C_{20}H_6Br_4O_3(OC_2H_5)(OK)$ .

**PRIMEROSE A L'ALCOOL; EOSIN, SOLUBLE IN SPIRIT; EOSIN S; EOSIN B B; ETHYLEOSIN; ROSE J B À L'ALCOOL.**

Primrose is the ethyl-ether of Eosin, and is obtained by ethylating Eosin. It forms a brown powder, and closely resembles Erythrin (Methyleosin). The shade is more bluish.



**DIANTHIN G; PYROSIN J; JAUNE D'ORIENT. IODOEOSIN.**

Erythrosin G is an alkali salt of diiodofluorescein, produced by the action of iodine on Fluorescein.

Brownish powder; aqueous solution, red, without showing a fluorescence; HCl, brown-yellow precipitate; NaOH, soluble red precipitate; solution in  $H_2SO_4$ , yellow; on diluting, brown-yellow precipitate.

Erythrosin G closely resembles the following dyestuff; but it possesses a more yellowish shade.

**ERYTHROSIN.**  $C_{20}H_6O_3I_4(ONa)_2$ .

**ERYTHROSIN B or D; EOSIN, BLUISH; EOSIN B or J; PRIMROSE, SOLUBLE; DIANTHIN B; PYROSIN B; IODOEOSIN B; ROSE B À L'EAU.**

Erythrosin is an alkaline salt of tetraiodofluorescein, and is obtained analogously to Eosin.

Brown powder; aqueous solution, cherry-red, without fluorescence; HCl, orange flocculent precipitate; NaOH, soluble red precipitate; solution in  $H_2SO_4$ , yellow; on diluting, brown-yellow precipitate.

Erythrosin dyes a very bright bluish-red, similar to Primrose, but richer in tinctorial powers. It is used like Eosin on the various textile fibres.

**EOSIN BN or SAFROSIN.**  $C_{20}H_6O_3Br_2(NO_2)_2(OK)_2$ .

**EOSIN SCARLET B; METHYLEOSIN; ECARLATE.**

Eosin BN is the potassium salt of dibromdinitrofluorescein, and is obtained by the action of nitric acid and bromine on Fluorescein.

Dark olive-brown powder; aqueous solution, yellowish-red, with a faint dark green fluorescence; HCl, yellow precipitate; NaOH, no change; solution in  $H_2SO_4$ , yellow; on diluting, yellow precipitate.

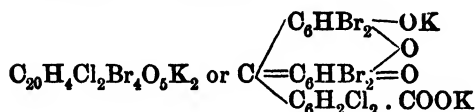
Eosin BN dyes a bluish-red shade similar to Erythrosin, but less bright. It is more suitable for wool than for silk dyeing, and is slightly faster to light and milling than most of the other Eosins.

Various mixtures of Eosin BN with other dyestuffs formerly have been brought into the market, and were used quite extensively in wool dyeing.

**LUTECIENNE** is a mixture of salts of tetranitrofluorescein, dinitrofluorescein, and Orange II.

**NOPALIN, IMPERIAL RED, and COCCIN** are similar mixtures containing dinitronaphthol (Naphthol yellow) and Aurantia.

**PHLOXIN** or **PHLOXIN P.** **ERYTHROSIN B B.**



Phloxin is an alkali salt of tetrabromdichlorfluorescein, and is produced by the action of bromine on dichlorphthalic anhydride.

Brownish-yellow powder; aqueous solution, red, with a yellowish-green fluorescence; HCl, orange-yellow precipitate; NaOH, no change; solution in H<sub>2</sub>SO<sub>4</sub>, yellow; on diluting, reddish precipitate.

Phloxin dyes a beautiful bluish-red shade, bluer than Erythrosin.

**CYANOSIN.** C<sub>20</sub>H<sub>4</sub>Cl<sub>2</sub>Br<sub>4</sub>O<sub>8</sub>(OCH<sub>3</sub>)<sub>2</sub>(OK).

Cyanosin or methylphloxin is produced by methylating Phloxin.

Brownish-red powder, sparingly soluble in water, freely soluble in dilute alcohol with a crimson colour, and a reddish-yellow fluorescence; HCl, destroys the fluorescence of this solution; NaOH, has no action; solution in H<sub>2</sub>SO<sub>4</sub>, yellow; on diluting, yellowish-red precipitate.

Cyanosin dyes a much brighter and bluer shade than Phloxin.

**ROSE BENGAL.** C<sub>20</sub>H<sub>4</sub>Cl<sub>2</sub>I<sub>4</sub>O<sub>3</sub>(OK)<sub>2</sub>.

This is the potassium salt of tetraiododichlorfluorescein, and is produced by the action of iodine on dichlorfluorescein.

Dark red powder; aqueous solution, bluish-red without fluorescence; HCl, orange-yellow flocculent precipitate; NaOH, finely-divided crimson precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, dark yellow; on diluting, dark orange flocculent precipitate.

Rose bengale dyes a more bluish-red than any of the preceding dyestuffs of this group.

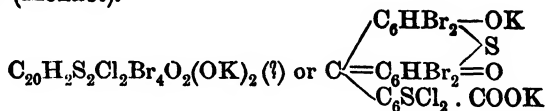
**PHLOXIN TA,** C<sub>20</sub>H<sub>2</sub>Cl<sub>4</sub>Br<sub>4</sub>O<sub>8</sub>(ONa)<sub>2</sub>;

**CYANOSIN B,** C<sub>20</sub>H<sub>2</sub>Cl<sub>4</sub>Br<sub>4</sub>O<sub>8</sub>(OCH<sub>3</sub>)<sub>2</sub>(ONa); and

**ROSE BENGAL B,** C<sub>20</sub>H<sub>2</sub>Cl<sub>4</sub>I<sub>4</sub>O<sub>3</sub>(OK)<sub>2</sub>.

These are obtained from tetrachlorphthalic anhydride, analogously to Phloxin, Cyanosin, and Rose bengale from dichlorphthalic anhydride. They form red powders, and resemble in their general properties these dyestuffs. They dye slightly more bluish shades.

**CYCLAMIN** (Monnet).

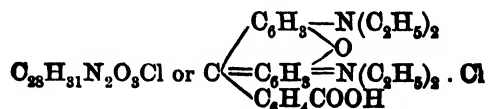


Cyclamin is probably a sulphur derivative of Fluorescein produced by treating dichlorfluorescein, first with sodium sulphide, and, subsequently, with bromine.

Bluish-red powder; aqueous solution, magenta-red without fluorescence; HCl, scarlet precipitate; NaOH, no change; solution in H<sub>2</sub>SO<sub>4</sub>, orange; on diluting, red flocculent precipitate.

Cyclamin is applied like the Eosins, and produces a beautiful very blue shade of red which resembles the colour of the blossoms of the ordinary wild *Cyclamen*.

**RHODAMINE B** (B.A.S.F., Ch. Ind. Basle). **ROSAZEINE B.** **SAFRANILINE.**

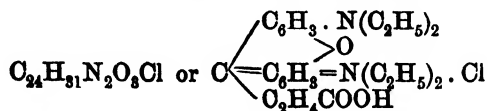






*Application and Properties.*—Same as Rhodamine 6 G and Irisamine G. The shade, however, is very much more yellowish and less bright, and is that of a yellowish-scarlet.

**RHODAMINE S** (B.A.S.F., Bayer, Soc. Chem. Ind.).



Rhodamine S is the basic hydrochloride of the succinein of diethylmetaminophenol, and is obtained analogously to Rhodamine B by heating succinic anhydride,  $\text{C}_2\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{O} \\ \text{CO} \end{smallmatrix}$ , with diethylmetaminophenol. It is similar to Rhodamine B.

Green crystals or bronzy or blackish-brown powder; aqueous solution, magenta-red, with a brownish fluorescence which disappears on heating; in alcohol sparingly soluble, with an intense yellow fluorescence; HCl, makes the solution more yellowish; NaOH, precipitates the colour-base as crimson flakes; solution in  $\text{H}_2\text{SO}_4$ , brownish, with a very strong green fluorescence; on diluting, red solution.

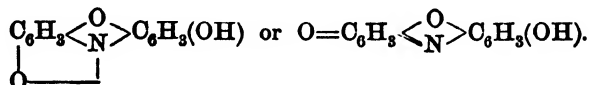
*Application.*—Rhodamine S possesses considerable affinity for unmordanted cotton, and is suitable for dyeing cotton, and cotton and silk mixed goods without the aid of mordants. It dyes a slightly yellower pink than Rhodamine B and G, but more bluish than "6 G." The dye-bath is prepared with the colour solution, and 1 or 2 parts of acetic acid for 1,000 parts of water. The material is worked in this bath until the desired shade is obtained. For cotton, which should be bleached and hot soaped before dyeing, the temperature is raised to 35° to 45°; mixed goods are dyed without heating. Rhodamine S is useful for shading direct cotton colours by topping. It may also be dyed on tannin-mordanted cotton on which brighter and more yellowish shades are obtained than with Rhodamine B. It is best to fix the tannin with acetate of alumina instead of with antimony salts the shades coming out more yellowish and brighter with the former.

#### ADDENDUM:

**RESORCIN BLUE (FLUORESCENT BLUE)** (Soc. Chem. Ind., Sandoz). **IRIS BLUE** (B.A.S.F.).



Resorcin blue is the ammonium compound of tetrabromresorufin and is obtained by heating resorufin in alkaline solution with bromine. Resorufin ( $\text{C}_{12}\text{H}_7\text{NO}_3$ ) is obtained by the action of nitrous acid on resorcin, and is thus constituted:—



Resorcin blue comes into commerce as an olive-brown liquid which contains small green crystals. The mass dissolves in water with a violet colour; hydrochloric acid produces a brownish precipitate; caustic soda forms a red-violet precipitate, while the solution becomes red-violet with a brownish-yellow fluorescence. The dry substance dissolves in sulphuric acid with a blue-violet colour, which becomes, on diluting with water, at first red-violet and then a brown-orange precipitate separates out.

*Application.*—Resorcin blue is not dyed on cotton. It is not much used for wool dyeing, but is employed on silk. It dyes this fibre with a blue-violet colour and a remarkable reddish fluorescence which is seen very prominently by gaslight; when used in combination with other colouring matters it gives pleasing shades, all possessing fluorescence. The shade is very fast to light, washing, and acids.

*Silk* is dyed in a boiled-off liquor bath which has been slightly acidulated with acetic acid, and is brightened with acetic, tartaric, or sulphuric acid.

## ACID COLOURS.

(See also under *Direct Cotton Colours*, *Acid Chrome Colours*, and *Mordant Colours*.)

The distinction of the acid colours as a separate group is based on practical requirements, not on strictly scientific principles. On the one hand, there is no sharp line of demarcation between them and the direct cotton colours, and on the other hand, the acid colours, acid chrome colours and mordant colours are frequently related to each other, a number of dyestuffs belonging practically to two of these groups or even to all of them, as is, for instance, the case with Cotton yellow G. A few, like the Soluble blues, can also be dyed like the basic colours. The common characteristic property of the acid colours is that they are dyed on wool or silk in an acid bath and that they can be mixed with each other to produce compound shades.

In this chapter only those acid dyestuffs will be described which are principally dyed without the aid of metallic mordants on wool or silk, and which are usually termed "Acid Colours." Those which are fixed, as a rule, by after-chroming, like the Cloth reds, Alizarin yellows, Diamond blacks, &c., will be treated in a separate chapter as *Acid Chrome Colours*, while those which dye unmordanted cotton fairly fast to washing have been discussed under the heading of *Direct Cotton Colours*.

*N.B.*—The derivatives of Anthracene, like Alizarin saphirol, which dye in an acid bath, will be treated together with the other Anthracene colours under the heading *Mordant Colours*.

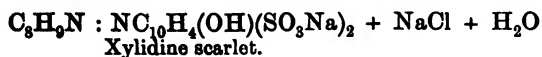
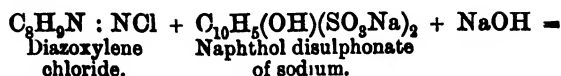
The acid colours may be divided into three groups according to their origin and chemical constitution.

1. Nitro-compounds.
2. Azo-compounds.
3. Sulphonated basic colours.

The first group, the nitro-compounds, owe both their acid character and their tinctorial properties to the presence of several nitro-groups in their molecule. In addition to the "chromophorous" nitro-groups they contain, as "auxochromous" groups, hydroxyl (OH)—*e.g.*, Picric acid,  $C_6H_2(NO_2)_3(OH)$ , or the imino-group (NH), as in Aurantia  $[C_6H_2(NO_2)_3]_2(NH)$ , a dyestuff now disappeared from the market. The nitro-compounds are prepared by the action of nitric acid on certain phenols, such as phenol or naphthol; or on secondary aromatic amines—*e.g.*, diphenylamine. With the exception of Naphthol yellow S, none of these dyestuffs are sulphonated compounds. Like the other acid colours the commercial products are sold in the form of their alkaline salts (Picric acid excepted).

The second group, the azo-compounds, are, without exception, sulphonic acids of amino- or oxyazo-compounds, the azo-group ( $-N=N-$ ) being the chromophor and the group (NH<sub>2</sub>) or (OH) respectively, the auxochromous group. The acid azo-colours are produced by combining diazotised aromatic

amines and their sulphonic acids with aromatic amines or phenols or their sulphonic acids, *e.g.* :—



The acid azo-colours contain one or several azo-groups; some of the tetrazo-compounds also belong to this class, and, generally speaking, the latter cannot be strictly divided into acid colours and direct cotton colours, since most of the tetrazo-colours can be dyed on the animal fibres by the same methods as the true acid colours, although not always with satisfactory results.

The third group consists of the sulphonic acids of certain bases which are colouring matters by themselves, and contain both the chromophorous and the auxochromous groups. The bases are sometimes employed as basic dyestuffs—*e.g.*, Magenta or Aniline blue; in most cases, however, their insolubility in water, cost of production, or other causes, prevent their application in dyeing without being sulphonated, as is the case with the bases of the Acid greens and Acid violets, &c. The chromophors of this group are generally in accordance with the origin of the dyestuffs, the same as those of the basic colours. Most of these dyestuffs are derivatives of triphenylmethane; notable exceptions are Tartrazin, Quinoline yellow, Thio-carmin, and the Indulines and Rosindulines. By the entrance of the sulpho-group into the basic compound an acid character is imparted to the latter, and the tinctorial properties become correspondingly changed. The shade remains about the same, but the fastness to light is increased. In addition, the dyestuffs lose by sulphonating the property of forming lakes with tannic acid, and cannot be fixed on cotton or linen like the original substances; for their fixation on the animal fibres an acid bath is required.

The various acid colours are sold in the form of their alkali salts; a few—*e.g.*, the Patent blues—in the form of their lime salts. Picric acid is an exception; it is sold in the free state, owing to the picrates being explosive substances.

The acid colours are decolourised by the action of acid reducing agents, but they are affected in very different ways. The nitro-compounds are converted into amino-compounds, from which the original colouring matter cannot be regenerated. The azo-compounds are decomposed by the breaking up of the azo-group and cannot be linked together again in a simple manner. Lastly, most of the dyestuffs of the third group form leuco-compounds, from which the original colouring matter is more or less easily regenerated by oxidation.

**Methods of Dyeing with the Acid Colours.**—The acid colours, with very few exceptions, cannot be fixed on cotton or linen so as to resist washing. If precipitated in these fibres as metallic lakes with the aid of salts of aluminium, tin, &c. (similarly to the mordant colours), the lakes are decomposed by water and the colour is extracted. The Soluble blues or Cotton blues resist water slightly better. Of the other acid colours the Crocein scarlets and allied colours only—*i.e.*, the azo-compounds prepared by combination of amidoazo-benzene or amidoazotoluene with betanaphthol sulphonic acid (B.), or the so-called gamma acid, or alphanaphthol disulphonic acid (Sch.)—are of some importance in cotton dyeing since they resist light better than the benzidine colours and are not sensitive to acids. For this reason they are still employed in cotton dyeing in spite of their inferior fastness to washing. The acid colours have never been used to any large extent in the dyeing of linen, but they find application on jute.

It is principally the wool fibre on which the acid colours find application, and on this material they are dyed to a very great extent, owing to the simplicity of their application and the comparatively permanent character of the shades obtained; the wool fibre possesses a natural affinity for acid colours, acting as a base and forming more or less insoluble lakes with them. For the fixation of the acid colours on wool an acid bath is required, and this fact is usually explained by the supposition that the acid is necessary to set the colour acid at liberty and to enable it to combine with the wool. From investigations made on this subject,\* however, it appears that the acid which is added to the dye-bath not only acts on the dyestuff, but also chemically changes a portion of the wool so as to render it capable of combining with the colour acid. Wool was boiled with 10 per cent. of its own weight of sulphuric acid and then boiled out 9 times with 100 times its own weight of distilled water, until the water was absolutely neutral to Methyl orange. In dyeing with 2 per cent. Crystal scarlet *without* any addition of acid, the wool showed a considerably fuller and more even shade than another pattern dyed with 2 per cent. of the same dyed with an addition of 2½ per cent. sulphuric acid. On the other hand, if the dye-bath was made up with sufficient sulphuric acid to neutralise the sodium in the dye—0.2 per cent. sulphuric acid for 2 per cent. Crystal scarlet—a light shade only was obtained; nor was double this amount sufficient to produce a full shade, and practical experience has shown that the minimum amount necessary is 2 to 4 per cent., or from 20 to 40 times as much as would be necessary to liberate the free colour acid. (See also Sisley, *Journ. Soc. Dyers and Col.*, 1908, p. 251.)

The acid colours also possess great importance for silk although most of them cannot be fixed on silk fast to washing. It seems that the basic properties of the silk fibre are too feeble to render it capable of forming stable compounds with the colour acids, and that the combinations which are formed between the two substances are decomposed by water.

The acid colours produce beautiful and delicate hues, but they do not possess great tinctorial power. For a full shade on wool, in most cases about 2 to 4 per cent. of colour are required.

The acid colours vary in fastness to light; many of them are very fast and a great number resist light fairly well. Their resistance towards other influences, such as washing, milling, or rubbing, as a rule, is greatest on wool, but varies even on this fibre.

*Dissolving of the Colours.*—The acid colours dissolve (with a few exceptions) freely in hot water, and require about 25 to 50 times their own weight of water for solution. It is best to use distilled water, although, as a rule, hard water is not so injurious in the dyeing with the acid colours as with most other dyestuffs, because the dyeing proceeds in an acid bath, and the lime-lake which may have been formed is afterwards decomposed by the acid. The colours should be well dissolved in boiling water, and the solutions filtered before use.

The colours may be dissolved in tin vessels without injurious effect. It must be noted, however, that most of these dyestuffs are reduced by stannous salts, and, therefore, the *acidified* solutions of the colours should not be in contact with tin, and the dyeing should not take place in tinned vessels.

The methods which are best suited for the application of the different dyestuffs are indicated in the special descriptions; in the following are given various methods which are more or less generally employed:—

**Dyeing of Cotton with the Acid Colours.**—The dye-bath is used as concentrated as possible to produce full shades; it is never exhausted by the cotton. Both the mordant- and dye-liquors are used continuously and freshened

\* *Journ. Soc. Dyers and Col.*, 1888, p. 107.



up regularly. The shades which are produced by any one of these methods are not fast even to a light soaping, but they resist light moderately well.

*First Method.*—The dye-bath is made up with common salt to stand at 5° to 7° Tw., and an excess of colouring matter is added. The goods are worked in the hot solution and dried without washing. Light and fugitive shades only can be produced in this way.

*Second Method.*—Cotton is impregnated with a solution of soap, to which some gelatine has been added, and dyed without washing. (This preparation with soap and gelatine is frequently omitted.) The dye-bath is prepared with 10 per cent. of alum and 1 per cent. of acetic acid (of the weight of the goods) and kept very concentrated, common salt being added with advantage; the temperature is gradually raised to the boiling point, and finally the goods are dried without washing. The colour is not at all fast to washing, and resists the action of light less than when dyed by one of the following methods.

*Third Method.*—Cotton is mordanted in a bath of basic alum which has been prepared by dissolving 1 kg. (1 lb.) of alum, and  $\frac{1}{2}$  kg. ( $\frac{1}{2}$  lb.) of soda crystals, in 200 litres (20 galls.) of water for every 10 kgs. (10 lbs.) of cotton. The goods are worked for half an hour in this bath and then allowed to soak three to five hours longer, wrung out and dyed (without washing) in a separate dye-bath at 40° to 50°; after 45 minutes working they are taken from the bath, wrung out, and dried without washing. The cotton may be impregnated with tannin before it is mordanted with alum; it is said that the shades thereby become faster to washing.

*Fourth Method.*—The cotton is steeped for two to three hours in a lukewarm bath, prepared by dissolving  $\frac{1}{2}$  kg. ( $\frac{1}{2}$  lb.) of stannate of soda in 200 litres (20 galls.) of water for every 10 kgs. (10 lbs.) of cotton, wrung out, and steeped for two hours in a bath of basic alum. The preparation of the alum-bath and the subsequent dyeing proceed exactly as in the previous method.

*Fifth Method.*—The cotton is soaped in a warm soap-bath to which some gelatine has been added, and worked for half an hour in a cold bath of stannic chloride, wrung, and worked for another half-hour in a bath of basic alum prepared as before. It is then dyed as by the previous methods.

Several colouring matters, notably Biebrich scarlet, Fast red A, and Azococcin 2 R, form insoluble precipitates with alum; before dyeing cotton which has been mordanted with alum in such dye-tuffs it should be rinsed in cold water, and some acetic acid should be added to the dye-bath.

Many attempts have been made to *animalise* the cotton in order to make it take up the acid dyes like wool and silk, but so far no process has been devised which is of any practical importance. Of the methods proposed, the following may be mentioned:—Treatment with tannic acid and, subsequently, with gelatine; impregnating with albumen solution and steaming; impregnating with a solution of wool in caustic soda, and, subsequently, passing through dilute sulphuric acid. It is remarkable that cotton steeped for several hours in strong nitric acid acquires an affinity for acid colours (*Knecht*).

Linen can be dyed with the acid colours in precisely the same way as cotton, but it requires faster shades than can be obtained with these materials.

*Dyeing of Jute with the Acid Colours.*—As little acid as possible, preferably acetic acid, is used for the dyeing of jute with the acid colours. Instead of acetic acid, alum or aluminium sulphate is frequently used; 2 per cent. acetic acid or 2 to 5 per cent. alum is added to the dye liquor and the jute is dyed at the boil. In the case of dyeing with colours, the free acid of which is very soluble, jute is mordanted with basic alum; if the colour acid is not freely soluble no mordanting is necessary; often some alum is added to the dye-bath.

The acid colours are less important for the dyeing of jute than the basic

colours, but many of the former are frequently used owing to their better fastness to light.

**Dyeing of Wool with the Acid Colours—First Method.**—The simplest and most generally employed process of dyeing wool with the acid colours is to prepare the dye-bath with the required amount of dyestuff, 2 to 4 per cent. of sulphuric acid, and 10 to 30 per cent. Glaubersalt, or with 5 to 10 per cent. sodium bisulphate, and to dye the wool in this bath, boiling three-quarters to one hour. With many dyestuffs it is not admissible to enter the goods at the boil as the colours would come out very uneven, and it is necessary to commence dyeing at 70° or even at 40° only, raising the temperature gradually within 20 to 40 minutes to the boil and boiling 45 minutes. With other dyestuffs it is of no advantage to gradually heat the bath because they are not fixed except at or near the boiling temperature, or they level well on prolonged dyeing. When using this class of dyestuffs, usually called *levelling dyestuffs*, the bath is prepared with all its ingredients, and the wool is entered into the hot or boiling bath and dyed at the boil for about one hour, until the liquor is well exhausted and the colour evenly fixed.

Prolonged boiling is necessary with all colours to fix them well, and, as has been indicated, the levelness is improved in many, but not in all, cases by continued boiling.

Glaubersalt exerts a levelling influence. Probably it retards the fixation of the colours; it may also dissolve the colours when deposited in excess on some parts of the material and enable them to be fixed on other parts of the material, it being a fact that the acid colours are stripped off the material by a weak solution of sulphate of soda much more readily than by water or by a weak acid solution.\* Sodium bisulphate is frequently used in place of the mixture of sodium sulphate and sulphuric acid, as it acts still better than this mixture in producing levelness. This is usually explained by the fact that the bisulphate is only gradually dissociated in the liquor into acid and sodium sulphate, and therefore exerts its acidifying action more gradually than the free acid.

**Second Method.**—Another way, which, however, requires more time and therefore is rarely used, is to introduce the material into the warm bath, to which has been added the required amount of colouring matter, to heat up to the boiling point, and gradually add the sulphuric acid in small portions to the *boiling* bath, turning frequently all the time. In place of sulphuric acid alone a mixture of 2 to 5 per cent. of sulphuric acid and 10 to 30 per cent. of Glaubersalt, or, better, 5 to 10 per cent. of bisulphate of soda can be used. The method of adding the colour solution gradually in several small portions to the bath is not so well adapted to produce even shades in the dyeing with these colouring matters as with the basic colours.

**Third Method.**—More brilliant colours are produced by making up the dye-bath with the colour solution and 5 to 8 per cent. bisulphate (or 2 to 3 per cent. sulphuric acid and 10 per cent. Glaubersalt), and adding either 1 to 1½ per cent. stannic chloride (60° Tw.) or 6 to 8 per cent. alum; the wool is introduced at 40°, and the bath heated more or less rapidly to the boil, and kept boiling as long as required.

Since the azo-colours are reduced and destroyed by stannous chloride, the presence of this compound in the tin solution must be strictly avoided.

**Fourth Method.**—This method differs from the first one by the partial or entire substitution of sulphuric acid by the milder acting acetic acid, which causes the dyestuffs to dye more slowly. Also it does not exert a detrimental

\* The coal-tar dyestuffs of the Farbwerke, vorm. Meister, Lucius & Brüning, Hoechst M., 1896, p. 7. A. W. Hallit, *Journ. Soc. Dyers and Col.*, 1899, p. 30. E. Knecht, *ibid.*, 1905, p. 250.

action, as sulphuric acid does on the shade of certain dyestuffs, while some which are precipitated from aqueous solution by sulphuric acid are not so affected by acetic acid. 5 to 10 per cent. acetic acid 1.06 specific gravity (12° Tw.) are used, together with 10 to 20 per cent. Glaubersalt, and are added to the dye liquor either before entering the goods or after some boiling. Frequently the bath is finally exhausted by the addition of about 2 per cent. sulphuric acid.

More recently acetic acid is frequently replaced by formic acid, which holds an intermediate position in its action between acetic and sulphuric acids.

*Fifth Method.*—Dyestuffs which dye very rapidly and unevenly are dyed with advantage with the addition of ammonium acetate. This salt impedes the dyeing of the acid colours; but on prolonged dyeing it is dissociated, the ammonia is driven off, and acetic acid is very gradually liberated in the dye-liquor. Thus very good results are obtained with colours which are otherwise very difficult to dye level. The bath is prepared with 5 to 10 per cent. ammonium acetate (of the commercial solution), the colour solution is added, and the wool boiled in this bath for two and a-half hours. After this time 5 to 10 per cent. acetic acid is added to develop the shade completely, and frequently, after a little while, 1 to 2 per cent. sulphuric acid are also added to exhaust the bath. If the bath is to be used continuously it is neutralised before the next operation with ammonia.

Instead of ammonium acetate, ammonium sulphate can be used. This salt decomposes slowly on boiling, ammonia is driven off with the steam and sulphuric acid is liberated very gradually in the dye-liquor. The bath is made up with 20 to 25 kgs. (20 to 25 lbs.) ammonium sulphate for 1,000 litres (100 galls.) of dye-liquor, the colour solution is added and the wool boiled in this bath for two and a-half hours. After this time the bath is generally sufficiently acid for dyeing with all other acid colours; sometimes it is better to add a little acetic acid to develop the shade completely. If the bath is to be used continuously it is neutralised before the next operation with ammonia.

Although this method yields very level shades it is rarely used owing to the long time of boiling it requires.

The preceding method in its varying forms may also be used to dye well through thickly milled cloth or hard spun yarns which are difficult to penetrate.

When dyed on goods composed of wool and silk with the addition of ammonium acetate (without acid) the acid colours dye almost exclusively the wool, the silk remaining nearly colourless.

When wool dyed with acid colours is boiled for a short time only with acetate of ammonia, much colour is stripped since the acetate (as long as not decomposed) exerts a strong dissolving action.

*Sixth Method.*—Many acid colours dye wool fairly well in a boiling neutral bath, and may, therefore, be used to advantage for shading the wool in union goods when dyeing with direct cotton colours by the one-bath method (p. 386).

The fastness of the acid colouring matters to light, milling, &c., on wool differs greatly. Most of the acid greens and acid violets are fugitive to light, whereas many of the azo-colours are fairly fast or even very fast. Many of the colours resist soaping and milling fairly well; they are, however, generally stripped to some extent and liable to bleed, this defect being common to almost all direct-dyeing colours; by boiling with alkaline liquors they are removed from the fibre (see below). Some of the acid colours are prone to rub if the dye-bath is not exhausted; hence it is better in most cases not to use an excess of colouring matter; good rinsing of the material after dyeing will obviate this defect to some extent. As a rule the acid colours are not sensitive towards the action of dilute acid, most of them resist alkalies well; many, however, principally some of the third group, are decolourised or greatly altered by alkalies.

It is sometimes desirable to remove the colour from the fibre; the best way is to boil the goods in a solution of ammonium acetate which strips the colour slowly without damaging the material. By boiling the goods for fifteen or twenty minutes with a small quantity of soda ash or ammonia, the acid colours are removed more thoroughly and rapidly; but the wool fibre is always deteriorated to some extent by the alkaline liquor. After this treatment the material should be rinsed in water and, subsequently, boiled with some acid before it can be dyed again with acid colours.

More energetic stripping agents are sodium hydrosulphite and the formaldehyde compounds of hydrosulphite, especially the basic zinc sulphoxylate sold under the names of Hydrosulphite A Z (M.L.B.), Hyraldite Z for stripping (Cassella), Decroline (B.A.S.F.).

The material to be stripped is first treated in a weak solution of sodium carbonate or of ammonia, well rinsed, and then brought into a bath containing about  $2\frac{1}{2}$  to 3 per cent. of one of the above-named products and 3 to 4 per cent. formic acid or 2 to  $2\frac{1}{2}$  per cent. sulphuric acid. Enter at  $50^{\circ}$  C., heat slowly to the boil, and boil for half an hour. Then rinse well, at first in cold and then in boiling water. Carbonised shoddy may be lightly rinsed and then stripped without adding acid. The stripping is best done in wooden vessels.

Dyeing of Silk with the Acid Colours.—Silk is usually dyed with the acid colours in a bath containing about 25 per cent. (of the volume of the bath) boiled-off liquor, which is slightly or distinctly acidulated with sulphuric or acetic acid. Sometimes the colour solution is added at once to the bath and the goods dyed near the boil; in other cases, it is necessary to add the colour solution gradually or to heat the bath slowly. Sometimes silk is dyed with acid colours with the addition of acetic acid only, no boiled-off liquor being used. In this case, careful working is necessary to obtain even shades. Silk is usually dyed below the boiling temperature; the material is entered into the lukewarm bath, which is gradually heated to  $80^{\circ}$  or  $90^{\circ}$  C. After dyeing, the silk is washed in water, brightened with very dilute sulphuric, acetic, or tartaric acid, and dried without further washing.

Most colours do not dye silk so well at the boil as at or below  $90^{\circ}$  C. Thus, when dyeing wool and silk mixed goods (glorias, &c.) in a boiling bath containing only a moderate quantity of acid—best acetic acid—the colour principally or exclusively works on to the wool. The silk may then be dyed another shade in a fresh, cold, or lukewarm bath with basic colours or such acid colours which do not stain the wool very much.

Most acid colours are not fixed very well on silk; many of them, notably Picric acid, are removed even by washing with water; some, however, are very fast to water also on silk. It seems that silk possesses only slight affinity towards these compounds, the basic properties of the silk fibre being weaker than those of the wool fibre. The fastness towards other influences, and especially the fastness of the acid colours dyed on silk to light and air is generally about equal to that on wool.

#### PICRIC ACID. $C_6H_2(NO_2)_3OH$ .

Picric acid or symmetrical *trinitrophenol* is produced by the action of nitric acid on a solution of phenol in concentrated sulphuric acid. The product is purified by recrystallising from water.

Picric acid forms pale yellow crystals which melt at  $122.5^{\circ}$  and deflagrate on being heated rapidly. It is sparingly soluble in cold, more freely in hot water, and readily soluble in alcohol or ether. The solution has a greenish-yellow colour and a very bitter taste. Dilute HCl has no action on the solution; NaOH makes the aqueous solution dark yellow; solution in  $H_2SO_4$ , yellow; on diluting, light yellow.

Picric acid is reduced by ammonium sulphide to *picraminic acid*. By

complete reduction it is converted into colourless *triamidophenol*, which is transformed by hydrochloric acid into diamidoquinoneimide hydrochloride, a blue substance. The alkali salts of picric acid crystallise well and are very strong explosives, especially the potassium salt.

*Application.*—Picric acid does not dye the vegetable fibres. It was formerly an important yellow dyestuff for the dyeing of silk and wool; but it has been almost completely replaced by the Naphthol yellows, Fast yellows, &c. Picric acid is still used in silk dyeing for its greenish-yellow shade and for its great tinctorial power. It is, however, extremely fugitive; soap, and even water, strips it from the fibre; and, by the action of air and light, it soon becomes dull and brownish. In addition, the colour is volatile, and sublimes slowly from the fibre even at the ordinary summer temperature. It is little used as a self-colour, but principally for shading blues and greens. Picric acid converts the animal skin into leather, and at the same time dyes it yellow; it is therefore used for hardening transparent leather.

Wool is dyed with 1 to 5 per cent. of Picric acid and with the addition of 2 to 3 per cent. of sulphuric acid, or 6 to 7½ per cent. of alum. Enter cold, heat to the boil in fifteen minutes, and dye fifteen minutes at the boil; dry without rinsing. The bath is not exhausted. The greenish-yellow shade is not fast to water, soap, milling, or rubbing. Exposed to light it soon fades to a dull orange, which is little affected by further exposure.

Silk is dyed with the addition of 1 to 1½ per cent. sulphuric acid or 3 to 5 per cent. of acetic acid, or in a bath of acidulated boiled-off liquor. Enter cold, heat during one hour to 50° or 60°, and dry without rinsing. One-tenth per cent. of dyestuff gives a distinct straw-yellow tint, four-tenths per cent. lemon-yellow, and 1 to 1½ per cent. full greenish-yellow shades, which are also extremely fugitive.

**NAPHTHOL YELLOW. MARTIUS YELLOW.**  $C_{10}H_6(NO_2)_2(OH)$ .

**MANCHESTER YELLOW, NAPHTHALENE YELLOW, NAPHTHYLAMINE YELLOW, ANILINE YELLOW.**

Naphthol yellow is the sodium, or ammonium, or calcium salt of *dinitro-alphanaphthol*. It may be prepared by dissolving alphanaphthol in sulphuric acid, and treating the solution with nitric acid.

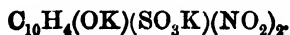
Yellow or orange tablets or crystalline powder; aqueous solution, golden yellow; HCl, light yellow precipitate; NaOH, soluble precipitate; solution in  $H_2SO_4$ , yellow; on diluting, light yellow precipitate. Dinitronaphthol, the acid of Naphthol yellow, melts at 138°, and forms by reduction diamino-naphthol. The dry sodium salt of dinitronaphthol explodes on heating, the ammonium salt burns off quietly.

*Application.*—Wool is dyed as with Picric acid. Less acid, however, is used, preferably 3 to 4 per cent. acetic acid, since an excess of acid gives rise to unevenness. Wool is also dyed in fairly deep shades from a neutral bath, and therefore this dyestuff is sometimes used for shading the wool when dyeing unions by the one-bath method.

Silk is also dyed as with Picric acid; the best way is to use a boiled-off liquor or soap-bath which has been acidulated with acetic acid. After dyeing, the silk is rinsed, brightened, and dried.

Naphthol yellow yields lemon-yellow to orange-yellow shades, which are not fast to milling or rubbing. The colour is moderately fast to air and light; it fades and becomes duller on exposure, but does not subsequently change much. The dyestuff is volatile and evaporates from the fibre, even at the ordinary summer temperature.

**NAPHTHOL YELLOW S. CITRONIN A; ACID YELLOW S or F Y.**



Naphthol yellow S is the potassium or sodium salt of the monosulphonic acid of Naphthol yellow (or dinitronaphthol). The potassium salt crystallises from water with  $1\frac{1}{2}$  mol. of water of crystallisation. The sodium salt is much more soluble in water. For its production alphanaphthol is converted into naphthol-trisulphonic acid by dissolving in fuming sulphuric acid, and to the solution nitric acid is added, which transforms the trisulphonic acid into dinitroalphanaphthol monosulphonic acid.

Light-yellow or orange-yellow powder; aqueous solution, yellow; HCl, makes the colour of the solution lighter without producing a precipitate; NaOH, no change; solution in  $H_2SO_4$ , yellow; on diluting, the solution becomes lighter without yielding a precipitate. The potassium salt of Naphthol yellow S is not readily soluble in cold water,\* but even very diluted solutions of the dyestuff are precipitated by caustic potash. The salt burns with scintillations on being heated on platinum.

Naphthol yellow S may be adulterated with the cheaper Naphthol yellow. The latter can be detected by adding hydrochloric acid to the aqueous solution; Naphthol yellow is precipitated or the solution becomes milky, whereas a solution of pure Naphthol yellow S remains clear. If the dry colour is treated with ether, Naphthol yellow S will not colour the same alone or on addition of soda, while the ether is coloured yellow by Naphthol yellow, and remains yellow on addition of soda.

*Application.*—Wool is dyed at the boil in an acid-bath with the addition of 5 per cent. of sodium bisulphate, or  $2\frac{1}{2}$  per cent. of sulphuric acid. Add the colour solution and the acid and dye at the boil (*Method I.*, p. 512), wash and dry. Naphthol yellow S dyes very level in a boiling bath.

Silk is dyed in a boiled-off liquor bath to which sufficient sulphuric acid has been added to produce an acid reaction. Add the colour solution, raise the temperature to the boiling point, work twenty-five to thirty minutes, wash, brighten, and dry.

Naphthol yellow S gives shades which are of a purer yellow than those of Naphthol yellow, slightly faster to light, fairly fast to soap, and good to acids and alkalis. It is not volatile, and does not evaporate from the fibre at a temperature below  $120^\circ$ .

Naphthol yellow S mixes well with all acid colours. Picric acid has been almost completely replaced by this dyestuff.

**QUINOLINE YELLOW** (Berlin, B.A.S.F., Bayer, M.L.B., Sandoz, Holliday, &c.).

Quinoline yellow is a mixture of the mono- and disulphonic acids of "Quinoline yellow, spirit soluble" or quinophthalone, a dyestuff used for colouring spirit varnish, &c., which is produced by heating quinaldine with phthalic anhydride and zinc chloride.

Dark yellow powder; aqueous solution, yellow; HCl, makes the solution paler; NaOH, makes it darker; solution in  $H_2SO_4$ , reddish-yellow; on diluting, light yellow.

*Application.*—Wool is dyed, like Naphthol yellow S, by *Method I.*, p. 512, and silk, according to p. 515, in acid liquors. Quinoline yellow dyes very bright greenish-yellows of very good fastness to light, acids, and alkalis, and fairly good fastness to washing. It has not much tinctorial power, but is an excellent substitute for Picric acid, and finds extensive application in silk dyeing.

**TARTRAZIN** (B.A.S.F., Ch. Ind. Basle).

**HYDRAZINE YELLOW. FLAVAZIN S. FAST LIGHT YELLOW G.**

Tartrazin is prepared by heating a solution of dioxytartaric acid with

\* See Knecht and Hibbert, *Journ. Soc. Dyers and Col.*, 1904, p. 249.

phenylhydrazine parasulphonate of sodium. It is destroyed by reducing agents, being resolved into sulphanilic acid and diamidosuccinic acid.

Orange-yellow powder; aqueous solution, yellow; HCl, the colour is rendered more intense; NaOH, has the same effect as HCl; solution in  $H_2SO_4$ , orange-yellow; on diluting, yellow.

*Application.*—Wool is dyed by *Method I*, p. 512, and silk, according to p. 515, in acid liquors. Tartrazin dyes a bright yellow, similar to flavin, which is very fast to light, fairly fast to washing, and good to acids and alkalis. It is, owing to its fastness and good levelling properties, one of the best acid yellows, and very extensively used, especially for all kinds of mixed shades in piece-dyeing.

FLAVAZIN L (M.L.B.), PYRAZIN YELLOW G G (Sandoz), and FAST LIGHT YELLOW 3 G (Bayer) are very similar to Tartrazin, and possess a still better fastness to light.

#### MILLING YELLOW O (Cassella).

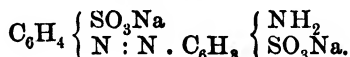
The constitution of this dyestuff is not known.

Yellow powder; aqueous solution, yellow; HCl, reddish-violet precipitate; NaOH, bright yellow precipitate; solution in  $H_2SO_4$ , crimson; on diluting, brownish precipitate.

*Application.*—Milling yellow O is dyed on wool in an acidulated bath with the addition of 10 per cent. sodium sulphate, and 2 to 3 per cent. acetic acid; after three-quarters of an hour's boiling the bath is exhausted by adding 2 to 4 per cent. acetic acid more. Milling yellow possesses excellent fastness to light, milling, acids, alkalis, and stoving, and is used for the production of fast and bright yellows and oranges on loose wool, yarns, and piece goods.

Silk is dyed also a very fast lemon-yellow in acidulated boiled-off liquor. Milling yellow is very fast to light and water on silk, also on tin-weighted silk.

#### FAST YELLOW G, S, or EXTRA, or ACID YELLOW G.



Fast yellow is the sodium disulphonate of aminoazobenzene, containing varying quantities of the monosulphonate; it is produced by the action of fuming sulphuric acid on aminoazobenzene (a yellow colouring matter).

Yellow powder; aqueous solution, yellow; HCl, red-orange; NaOH, causes no change; solution in  $H_2SO_4$ , brownish-yellow; on diluting, red.

*Application.*—Wool is dyed, like Naphthol yellow S, by the first method (p. 512), with the addition of sodium bisulphate or sulphuric acid to the bath. Dye, boiling for one hour, wash, and dry.

Fast yellow G dyes a shade similar to Flavin, which is fairly fast to light and washing. It is as fast to light as some of the best natural yellow colouring matters, but it is not very brilliant, and is sensitive to acids. The dyestuff is suitable for the dyeing of compound shades, since it is taken up very evenly by the wool fibre, and is chiefly used for golden yellow shades and for shading greens, olives, and browns.

Silk is dyed with Fast yellow in a boiled-off liquor bath, slightly acidulated with sulphuric acid. It can also be dyed without boiled-off liquor in a bath acidified with acetic acid. Add the colour gradually, work the yarn at the boil for half an hour, rinse, brighten with acetic or sulphuric acid, wash, and dry.

#### FAST YELLOW R.

Fast yellow R is produced analogously to Fast yellow G, by sulphonating amidoazotoluene.

Brown-yellow powder; aqueous solution, yellow; HCl, crimson; NaOH, no change; solution in  $H_2SO_4$ , yellowish-brown; on diluting, magenta-red.

**Application and Properties.**—Same as Fast yellow G. The shade is more orange-yellow.

**AZO-FLAVIN. INDIAN YELLOW.**

**NEW YELLOW, AZO-YELLOW, ACID AZO-YELLOW, CURCUMÉIN, CITRONIN.**

The dyestuffs which are sold under this great variety of names are not of a uniform composition. They are produced by the action of nitric acid on mixtures of diphenylamine orange and diphenylamine, and consist of more or less nitrated derivatives of these substances.

The commercial products vary also in their solubility; some dissolve readily, whereas others do not yield a clear solution. They show the following reactions:—Ochre-yellow powder; aqueous solution, yellow; HCl, dark red-brown or crimson precipitate or solution; NaOH, soluble brownish precipitate; solution in  $H_2SO_4$ , violet; on diluting, brownish solution or precipitate.

**Application.**—Same as Naphthol yellow S.

The different products level well, and produce reddish yellows which are fairly fast to light; they do not fade, becoming darker on exposure to light; they are also fairly fast to washing, and not sensitive to dilute acids or alkalis.

Azo-flavin is extensively used in wool and silk dyeing, especially for shading purposes, and is employed in the printing of wool and silk.

**DIPHENYLAMINE ORANGE.**

**ORANGE IV. ORANGE N, or M, or G S, TROPAEOLIN O O, NEW YELLOW, ACID YELLOW D, DIPHENYL ORANGE.**

Sulphanilic acid—diphenylamine.

Diphenylamine orange is produced by combining diazotised sulphanilic acid with diphenylamine, and converting the product into the sodium-salt.

Orange-yellow powder or tablets, not readily soluble in water; aqueous solution, orange-yellow; HCl, grey precipitate and red-violet solution; NaOH, soluble light yellow precipitate; solution in  $H_2SO_4$ , blue-violet; on diluting, purplish precipitate.

**Application.**—Same as Naphthol yellow S.

Diphenylamine orange has great tinctorial power. It dyes a yellowish-orange shade, which is fairly fast to light and washing, and not sensitive to alkalis. Acids turn the shade blue-violet.

This dyestuff levels very well, and is extensively used, especially for shading purposes, on wool and on silk.

**BRILLIANT YELLOW S.  $C_{18}H_{15}N_3(SO_3Na)_2$ .**

This product is a sulfonated diphenylamine orange, and is produced by the action of sulphuric acid on that colouring matter.

Orange-yellow powder; aqueous solution, yellow; HCl, violet-red; NaOH, no change or violet-red solution; solution in  $H_2SO_4$ , bluish-red; on diluting, crimson.

**Application.**—Same as Naphthol yellow S.

It dyes a redder and more brilliant shade of yellow than Fast yellow, but less red than diphenylamine orange, and is not sensitive to dilute acids.

**METANIL YELLOW.**

**TROPAEOLIN G, ORANGE M N, VICTORIA-YELLOW.**

Metanilic acid—diphenylamine.

Brownish-yellow powder; aqueous solution, orange-yellow; HCl, purplish solution and dark flocculent precipitate; NaOH, no change; solution in  $H_2SO_4$ , violet; on diluting, purplish.



*Application.*—Same as Naphthol yellow S. The shade is redder and more brilliant than that of Fast yellow G. It is rather sensitive to acids, and, before matching, it should be well rinsed. The shade is fairly fast to light and washing, and good to alkalis.

Metanil yellow levels well, and is principally used in wool dyeing as a self-colour and for shading yellowish-browns, olives, and blacks.

#### CHRYSOÏN or TROPAEOLIN R.

RESORCIN YELLOW TROPAEOLIN O, GOLDEN YELLOW, AKME YELLOW, YELLOW T, CHRYSÉOLIN.

Sulphanilic acid—resorcin.

Brown powder; aqueous solution, orange yellow; HCl, no change; NaOH, red-orange; solution in  $H_2SO_4$ , yellow; on diluting, orange-yellow.

*Application.*—Same as Naphthol yellow S. The shade is slightly redder than Fast yellow G; Chrysoïn is fairly fast to light and washing; it is not affected by acids, but is turned into a brownish-red by strong alkalis.

Chrysoïn dyes very evenly; it is principally used for compound shades in the dyeing of wool and silk. It is one of the fastest of these dyestuffs, but a rather expensive article.

#### ALPHANAPHTHOL ORANGE.

ORANGE I. or No. 1, TROPAEOLIN OOO No. 1.

Sulphanilic acid—alpha-naphthol.

Red-brown powder; aqueous solution, orange-red; HCl, brown precipitate; NaOH, cherry-red; solution in  $H_2SO_4$ , red-violet; on diluting, orange.

*Application.*—Same as Naphthol yellow S.

Alpha-naphthol orange dyes a red-orange shade, and possesses considerable tinctorial power. It has been used in wool-dyeing, but finds little application now.

Alphanaphthol orange is fairly fast to light; not quite so fast to washing and rubbing, and strongly reddened by dilute acids and alkalis.

#### ORANGE II. (or No. 2) or BETANAPHTHOL ORANGE.

TROPAEOLIN OOO No. 2, MANDARIN G EXTRA, GOLDEN ORANGE, ORANGE EXTRA, ORANGE G, CHRYSAUREIN, &c.

Sulphanilic acid—beta-naphthol.

Yellowish-red powder; aqueous solution, orange-yellow; HCl, dark orange precipitate; NaOH, brown-red; solution in  $H_2SO_4$ , crimson-red; on diluting, brown-yellow precipitate.

*Application.*—Wool and Silk are dyed with Orange II. in the same way as with Naphthol yellow S.

Orange II. dyes a reddish shade of orange, a little less reddish than Alpha-naphthol orange. It is fairly fast to light and washing, and is not sensitive either to acids or alkalis.

Orange II. levels well, and is very extensively employed in wool dyeing, both as a self-colour and in combination with other acid colours to produce browns and mode colours.

Cotton can also be dyed with Orange II.; the shade is moderately fast to light but not to washing. The methods indicated in the beginning of this chapter (p. 511) are employed.

#### ORANGE T or R. MANDARIN G R, KERMESIN ORANGE.

Orthotoluidine monosulphonic acid—beta-naphthol.

Brick-red powder; aqueous solution, reddish-orange; HCl, gelatinous yellowish-brown precipitate; NaOH, soluble brownish-orange precipitate; solution in  $H_2SO_4$ , crimson; on diluting, yellowish-brown precipitate.

*Application and Properties.*—Same as Orange II. The dyestuff strongly resembles Orange II., and can also be fixed like this on cotton. It is slightly redder in shade.

**ORANGE R** or **2 R**.

Xylidine monosulphonic acid—beta-naphthol.

Fiery-red powder; aqueous solution, orange-yellow; HCl, brown-red precipitate; NaOH, brown-yellow; solution in  $H_2SO_4$ , cherry-red; on diluting, brown-red precipitate.

*Application and Properties.*—Same as Orange II.; the shade is that of a yellowish-scarlet.

**ORANGE G** or **2 G**.

Aniline—beta-naphthol disulphonic acid (G salt).

Orange-red powder or crystalline leaflets; aqueous solution, orange-yellow; HCl, no change; NaOH, yellow-red; solution in  $H_2SO_4$ , orange-yellow; on diluting, no change.

*Application.*—Same as Naphthol yellow S.

Orange G dyes a yellow shade of orange, which is very fast to light and fairly fast to washing, faster than most of the other orange acid azo-colours, and is not sensitive to acids or alkalis. It dyes very evenly, and is principally used for the production of compound shades in wool dyeing.

**CROCEÏN ORANGE.** **PONCEAU 4 G B.** **BRILLIANT ORANGE G.**  
**PYROTIN ORANGE.** **ORANGE EN L** or **G R X.**

Aniline—beta-naphthol monosulphonic acid S.

Fiery-red powder; aqueous solution, orange-yellow; HCl, orange precipitate; NaOH, no change; solution in  $H_2SO_4$ , orange-yellow; on diluting, brownish-yellow precipitate.

*Application.*—Same as Beta-naphthol orange.

Crocein orange dyes a redder shade of orange than the preceding dyestuff, and possesses greater tinctorial power. The shade is very fast to light and fairly fast to washing, and not sensitive to dilute acids and alkalis.

Crocein orange is used for dyeing browns on wool and silk, and finds application for cotton dyeing; it is also employed for the production of lakes.

**BRILLIANT ORANGE O.** **ORANGE G T** or **R N.**

Toluidine—beta-naphthol monosulphonic acid.

Scarlet-red powder; aqueous solution, orange-yellow; HCl, brownish oil; NaOH, dark brown-red solution; solution in  $H_2SO_4$ , magenta-red; on diluting, brownish oil.

*Application.*—Same as Beta-naphthol orange. This dyestuff resembles Crocein orange.

**BRILLIANT ORANGE R.** **SCARLET R** or **G R.** **ORANGE N** or **X.**

Xylidine—beta-naphthol monosulphonic acid S.

Vermilion-red powder; aqueous solution, reddish-orange; HCl, brown-red precipitate; NaOH, no change; solution in  $H_2SO_4$ , cherry-red; on diluting, brown-red precipitate.

**Application.**—Same as Beta-naphthol orange. This dyestuff dyes a yellowish-scarlet or red-orange, redder than the two preceding dyestuffs, and closely resembles them. The product possesses good fastness to water, when dyed on silk, and is, therefore, used for producing yellowish-scarlets on silk.

**DOUBLE BRILLIANT SCARLET G (Berlin). ORANGE-RED I.**

Beta-naphthylamine sulphonic acid (Br.)—beta-naphthol.

Red-brown powder; aqueous solution, yellowish-red; HCl, brown precipitate; NaOH, soluble red-brown precipitate; solution in  $H_2SO_4$ , crimson; on diluting, brown-red precipitate.

**Application and Properties.**—Same as Orange II.

Double brilliant scarlet G dyes a yellow-scarlet shade.

**FAST ACID SCARLET (Durand).**

Beta-naphthylamine sulphonic acid\*—beta-naphthol.

Brick-red powder, sparingly soluble in water; aqueous solution, yellowish-red; HCl, soluble brownish precipitate; NaOH, makes the solution browner; solution in  $H_2SO_4$ , red-violet; on diluting, yellowish-red precipitate.

**Application.**—Wool and silk are dyed in acid-baths. Yellowish scarlets of fairly good fastness are produced by this dyestuff.

**SCARLET 2 G. BRILLIANT SCARLET 2 G.**

Aniline—beta-naphthol disulphonic acid (R salt).

Fiery-red powder; aqueous solution, reddish-orange; HCl, no change; NaOH, more yellowish; solution in  $H_2SO_4$ , cherry-red; on diluting, reddish-orange.

**Application and Properties.**—Same as Xylidine scarlets (see next page).

Scarlet 2 G dyes a reddish-orange; on prolonged exposure to light it becomes more yellowish.

**SCARLET R T, or R, or F R.**

Toluidine—beta-naphthol disulphonic acid (R salt).

Red powder; aqueous solution, yellowish-red; HCl, no change; NaOH, darker and more yellowish; solution in  $H_2SO_4$ , cherry-red; on diluting, yellowish-red.

**Application and Properties.**—Same as Xylidine scarlets (see next page).

The shade is more yellowish than scarlet 2 R.

**SCARLET 2 R or F 2 R (XYLIDINE SCARLET).**

Metaxylidine—beta-naphthol disulphonic acid (R salt).

Red powder; aqueous solution, yellowish-red; HCl, no change; NaOH, makes the solution darker and more yellowish; solution in  $H_2SO_4$ , cherry-red; on diluting, more yellowish.

**Application and Properties.**—See next page, *Xylidine scarlets*.

**SCARLET 3 R or 4 R. SCARLET F 3 R. (CUMIDINE SCARLET.)**

Pseudocumidine—beta-naphthol disulphonic acid (R salt).

For the production of Scarlet 4 R purified pseudocumidine or *amidotrimethylbenzene* is used; whereas Scarlet 3 R is prepared with crude pseudocumidine. A similar dyestuff, which shows the same reactions and is known under the same name, is obtained from amidodimethylethylbenzene.

\* Mixture of two isomeric sulphonic acids.

Scarlet 4 R is a dark red powder; aqueous solution, red; HCl, no change; NaOH, makes the solution more yellowish; solution in  $H_2SO_4$ , cherry-red; on diluting, red.

*Application and Properties.*—Same as Xylidine scarlets. The shade is bluer than that of Scarlet 3 R.

#### XYLIDINE SCARLETS (SCARLET R, 2 R, 3 R, and 4 R).

The scarlets (first introduced by the Farbwerke M.L.B.—Hoechst) which are produced by the reaction of diazotised metaxylydine and the homologous and isomeric bases are known as Xylidine scarlets or Scarlets R, 2 R, or 3 R, &c.

*Application of the Xylidine Scarlets.*—The Xylidine scarlets were the first azo-scarlets to be largely employed; they have rapidly replaced cochineal in the dye-house, owing to their low price and simple mode of application. They are less fast to light and to milling than cochineal, but in the brilliancy of their shades they are quite equal to, if not superior to, cochineal.

The Xylidine scarlets are used in enormous quantities for wool dyeing, very extensively for silk dyeing (like the azo-colours generally), and to a limited extent for cotton dyeing; on this last-mentioned fibre, however, they cannot be applied as well as Crocein scarlet and similar products.

Cotton is dyed by the methods given in the beginning of this chapter (p. 511). The Xylidine scarlets do not form precipitates with alum, and do not require precautions in this respect.

Wool is dyed with the Xylidine scarlets as with the other acid azo-colours (see *Method I.*, p. 512), with a gradual heating of the acid bath to the boil. They level moderately well, and are chiefly used as self-colours.

The Xylidine scarlets are fairly fast to light and washing, and fast to stoving, acids, and alkalis.

Silk is dyed with the Xylidine scarlets in an acidified bath of boiled-off liquor, and brightened with sulphuric acid. Acidulate the bath with sulphuric acid, add the colour solution, heat to the boil, and continue to boil for twenty-five to thirty minutes, rinse, brighten, and dry.

#### PALATINE SCARLET A (B.A.S.F.). COCHINEAL SCARLET P S (Bayer).

##### Xylidine—alpha-naphthol disulphonic acid R G.

Brown-red powder; aqueous solution, scarlet-red; HCl, gelatinous yellow-brown precipitate; NaOH, more yellowish. solution in  $H_2SO_4$ , bluish-red; on diluting, yellow-brown precipitate.

*Application.*—Same as Xylidine scarlets. Palatine scarlet dyes a scarlet similar to Xylidine scarlet 2 R, which, however, possesses greater brilliancy and is very fast to light (not inferior to cochineal in fastness to light). It is fairly fast to washing, and fast to stoving, acids, and alkalis. It levels fairly well, and is used to a great extent as a substitute for cochineal on piece goods.

PALATINE SCARLET 3 R and 4 R possess nearly the same, but more bluish reactions as the brand A, and dye more bluish shades of scarlet of almost the same fastness to light and equal fastness to milling, stoving, acids, and alkalis.

BRILLIANT COCHINEAL 2 R and 4 R (Cassella) closely resemble the Palatine scarlets in properties and shades, and are used for the same purposes.

##### BIEBRICH SCARLET.

SCARLET B, 3 R B, or E C, FAST SCARLET B, NEW RED L, IMPERIAL SCARLET.

##### Aminoazobenzene disulphonic acid—beta-naphthol.

Biebrich scarlet, introduced by Kalle & Co., was one of the first scarlets in the market

**Biebrich scarlet** is a brown-red powder; aqueous solution, orange-red; HCl, flocculent dark red precipitate; NaOH, brown-red precipitate, soluble with a violet colour; solution in  $H_2SO_4$ , green; on diluting, it turns from blue to red, and yields a brown-red precipitate.

**Biebrich scarlet** forms an insoluble precipitate with alum in contrast with the isomeric compound **Crocein 3 B**.

*Application.*—On wool and silk same as **Xylidine scarlet**. **Biebrich scarlet** dyes a bluish-scarlet which has a brownish tint. The colour resembles the **Xylidine scarlets** as regards fastness to light, washing, acids, and alkalis, but is not fast to stoving.

**Cotton** is dyed by the methods indicated in the beginning of this chapter (p. 511). The material should be washed in water after the mordanting with aluminium compounds, and the dye-bath should be slightly acidulated with acetic acid, to prevent the dyestuff from being precipitated by alumina in the dye-liquor.

**CROCEIN SCARLET 3 B** (Bayer, Kalle), **SCARLET 4 RB** (Berlin).

Aminoazobenzene monosulphonic acid—beta-naphthol sulphonic acid (B).

**Crocein scarlet** was the third of the scarlets which appeared in the market about a quarter of a century ago, and almost revolutionised the dyeing of red and mixed shades on wool. Its shade is purer than those of the **Xylidine** and **Biebrich scarlets**, and excelled only by the **Brilliant croceins**.

Red-brown powder; aqueous solution, scarlet-red; HCl, flocculent yellowish-brown precipitate; NaOH, soluble dirty violet-red precipitate; solution in  $H_2SO_4$ , blue; on diluting, the solution passes through violet to red and forms a dark red precipitate.

*Application.*—Same as **Xylidine scarlets**.

**Crocein scarlet** is slightly faster to washing on cotton than the **Xylidine scarlets**. Although greatly inferior to the direct cotton colours in fastness to washing, and almost entirely supplanted by them, it is still used for the Eastern trade, where fastness to light is required.

On wool **Crocein scarlet** dyes a very bright scarlet, which is superior to **Xylidine scarlet** in fastness to light and washing and in brilliancy, but does not level as well; it is fairly fast to light and milling, but not fast to stoving in contrast with the **Xylidine scarlets**.

On silk **Crocein scarlet** is of some value owing to its very good fastness to light.

**Crocein Scarlet R, B, and 2 B** are mixtures of **Crocein scarlet 3 B** with the **Oranges**.

**Crocein Scarlet 5 B** is a mixture of the **Crocein scarlets 3 B** and **7 B**.

**CROCEIN SCARLET 7 B or 8 B** (Bayer, Kalle). **PONCEAU 6 RB** (Berlin).

Aminoazotoluene monosulphonic acid—beta-naphthol sulphonic acid (B).

Dull red powder; aqueous solution, scarlet-red; HCl, little change, but the solution slowly becomes turbid; NaOH, soluble dirty violet precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet-red.

*Application and Properties.*—Same as **Crocein scarlet 3 B**. The shade is bluer; a pure bright red, almost crimson-red. It is suitable for compound shades in place of **Acid magenta**.

**CROCEIN SCARLET 3 BX** (Bayer). **COCCIN 2 B. SCARLET 000**.

Naphthionic acid—beta-naphthol monosulphonic acid (B).

Scarlet-red powder; aqueous solution, yellowish-red; HCl, no change

NaOH, yellowish-brown; solution in  $H_2SO_4$ , red-violet; on diluting, yellowish-red.

*Application.*—Same as Xylidine scarlets. Croceïn 3 B X resembles Croceïn 3 B in the appearance of shade, and in fastness it stands between Croceïn 3 B and the Xylidine scarlets. It dyes more level on wool than Croceïn 3 B, and is chiefly used for this fibre and for silk.

**BRILLIANT CROCEÏN M** (Cassella). **BRILLIANT CROCEÏN** (M.L.B., Bayer). **COTTON SCARLET** (B.A.S.F.). **COTTON SCARLET 3 B CONC.** (Kalle). **SCARLET B O EXTRA** (Berlin).

Aminoazobenzene—beta-naphthol disulphonic acid (G salt).

Light brown powder; aqueous solution, cherry-red; HCl, brown precipitate; NaOH, brown; solution in  $H_2SO_4$ , red-violet; on diluting, blue, then red solution and formation of a brownish precipitate

*Application.*—Same as Xylidine scarlets and Croceïn scarlets. Brilliant croceïn is very similar to Croceïn scarlet in fastness, and possesses a purer shade; it is the finest of all the scarlets, and is used for the dyeing of cotton, silk, wool, and other fibres, also for paper dyeing and lake making. It dyes a shade similar to Xylidine scarlet 3 R and Croceïn scarlet 3 B.

**BRILLIANT CROCEÏN 9 B** (Cassella).

Beta-naphthylamine gamma-disulphonic acid—azoanilino—  
beta-naphthol disulphonic acid (R and G salt).

Brown powder; aqueous solution, magenta-red; HCl, darker and bluer; NaOH, brown-red; solution in  $H_2SO_4$ , blue; on diluting, red-violet.

*Application.*—Same as Brilliant croceïn M, which it equals in fastness; the shade, however, is much more bluish and a little bluer than that of the following Croceïn A Z.

**CROCEÏN A Z** (Cassella).

Aminoazobenzene—alpha-naphthol disulphonic acid.

Brown powder; aqueous solution, red; HCl, makes the solution brownish; NaOH, crimson-red solution; solution in  $H_2SO_4$ , blue, and in transparent light, red-violet; on diluting, brown precipitate.

*Application.*—Same as Xylidine scarlet and Brilliant croceïn. Croceïn A Z dyes on the various fibres a bluish-red of very good fastness to light. It yields on cotton and jute much more intense shades than most other dyestuffs of this group, and is dyed on these fibres with the addition of 10 to 15 per cent. alum and an equal amount of Glaubersalt at 75° C. Wool is dyed fairly level and fairly fast to washing, and fast to acids and alkalis.

**BRILLIANT SCARLET 4 R** or **5 R** (Cassella, Bayer, Dahl). **COCHINEAL RED A** (B.A.S.F.). **NEW COCCIN** (Berlin, M.L.B.). **SCARLET 00000** (Holliday).

Naphthionic acid—beta-naphthol disulphonic acid (G salt).

Scarlet-red powder; aqueous solution, scarlet-red; HCl, no change; NaOH, dark orange; solution in  $H_2SO_4$ , dirty red-violet; on diluting, red.

*Application.*—Same as Xylidine scarlets. Brilliant scarlet 4 R dyes a very brilliant scarlet on wool and silk, which is fairly fast to light and washing, not sensitive to acids and alkalis, but not fast to stoving.

**CRYSTAL SCARLET (6 R)** (Cassella, B.A.S.F., Berlin).

Alpha-naphthylamine—beta-naphthol disulphonic acid (gamma acid).

Dark red crystals with a golden lustre; aqueous solution, red; HCl, slightly darker; NaOH, more yellowish; solution in  $H_2SO_4$ , blue; on diluting, red. The sodium salt crystallises with 7 molecules of water.

*Application.*—Same as Xylidine scarlets. Crystal scarlet resembles Brilliant scarlet 4 R and dyes a more bluish shade of scarlet.

**AZO-COCCIN 2 R** (Berlin). **DOUBLE SCARLET R** (Levinstein).

Xylidine—alpha-naphthol sulphonic acid N W.

Red-brown powder, not freely soluble in water; aqueous solution, red; HCl, red-brown precipitate; NaOH, brownish-yellow; solution in  $H_2SO_4$ , magenta-red; on diluting, brown-red precipitate.

*Application.*—Same as Xylidine scarlets.

Azo-coccin 2 R yields shades which are similar to Xylidine scarlet 2 R and 3 R, but less pure; it is faster to light, fairly fast to washing, and not sensitive to acids or alkalies, and is useful for silk dyeing owing to its fairly good fastness to water on silk. The dyestuff is precipitated by alum in the dye-liquor, and is sensitive against the action of metals.

**AZO-EOSIN** (Bayer).

Orthoanisidine—alpha-naphthol sulphonic acid N W.

Red-orange powder; aqueous solution, red; HCl, brownish-orange precipitate; NaOH, brownish-orange; solution in  $H_2SO_4$ , crimson-red; on diluting, brownish-orange precipitate.

*Application.*—Same as Xylidine scarlets.

Azo-eosin yields a scarlet shade on wool—slightly bluer than Croceïn 3 B, fairly fast to light and washing, and fast to acids, alkalies, and stoving.

**DOUBLE BRILLIANT SCARLET 3 R** or **DOUBLE SCARLET EXTRA S**.

Beta-naphthylamine sulphonic acid (Br)—

alpha-naphthol sulphonic acid N W.

Brown-red powder; aqueous solution, yellowish-red; HCl, yellowish-brown flocculent precipitate; NaOH, no change; solution in  $H_2SO_4$ , crimson; on diluting, yellowish-red.

*Application.*—Same as Xylidine scarlets.

Double brilliant scarlet dyes a very pure scarlet on wool, and resembles the preceding dyestuffs in fastness.

**PYROTIN R R O** (Dahl).

Beta-naphthylamine sulphonic acid (D)—

alpha-naphthol sulphonic acid N W.

Brown-red powder; aqueous solution, yellowish-red; HCl, more bluish; NaOH, more yellowish; solution in  $H_2SO_4$ , magenta-red; on diluting, red.

*Application.*—Same as Xylidine scarlets.

Pyrotin R R O is used in cotton and wool dyeing for the production of scarlet shades, and equals the preceding products in fastness.

**SCARLET 5 R** (M.L.B.). **ERYTHRIN X** (B.A.S.F.).

Aminoazobenzene—beta-naphthol trisulphonic acid.

Brown powder; aqueous solution, cherry-red; HCl, violet precipitate; NaOH, violet; solution in  $H_2SO_4$ , blue-violet; on diluting, red.

*Application.*—Same as Xylidine scarlets.

Scarlet 5 R dyes a bluish shade of scarlet on wool, which possesses good fastness to light.

**SCARLET 6 R** (M.L.B., B.A.S.F.).

Naphthionic acid—beta-naphthol trisulphonic acid.

Brown powder; aqueous solution, cherry-red; HCl, no change; NaOH, red-brown; solution in  $H_2SO_4$ , blue-violet; on diluting, magenta-red.

*Application.*—Same as Xylidine scarlet.

Scarlet 6 R is similar to the preceding dyestuff. It produces still bluer scarlet on wool.

#### COCHINEAL SCARLET G (Schoellkopf).

Aniline—alpha-naphthol sulphonic acid (Cl).

Brick-red powder; aqueous solution, yellowish-red; HCl, brown-red precipitate; NaOH, orange; solution in  $H_2SO_4$ , cherry-red; on diluting, brown-red precipitate.

*Application.*—Cochineal Scarlet G is applied like the Xylidine scarlets. The dyestuff forms insoluble precipitates with calcium and magnesium salts; hence calcareous water or—for cotton dyeing—salt containing much magnesium should be avoided or purified. Cochineal scarlet G dyes a yellow shade of scarlet, which is fairly fast to light, milling, and acids.

COCHINEAL SCARLET 2 R and 4 R are the orthotoluidine- or xylidine-compounds respectively, analogous to Cochineal scarlet G, and possess the same properties as this dyestuff, yielding, however, more bluish shades of scarlet.

#### CROCEIN SCARLET B and 3 B (Schoellkopf).

These two dyestuffs are obtained by the action of diazotised amidoazobenzene, or amidoazo-orthotoluene respectively, on (1) naphthol 4:8 disulphonic acid. They show nearly the same reactions.

Red powder (Scarlet B) or brown powder (Scarlet 3 B); aqueous solution, bluish-red; HCl, violet precipitate; NaOH, violet; solution in  $H_2SO_4$ , violet; on diluting, violet precipitate.

*Application.*—Same as Xylidine scarlets and Crocein scarlets.

These two Crocein scarlets are used to some extent in the United States for cotton dyeing. They produce on this fibre bluish-red shades, which are equal to the Crocein scarlets (Bayer) in fastness to light and washing.

#### WOOL SCARLET R (Schoellkopf).

Xylidine—(1) naphthol 4:8 disulphonic acid.

Brown-red powder; aqueous solution, yellowish-red; HCl, bluish-red; NaOH, red-orange; solution in  $H_2SO_4$ , cherry-red; on diluting, red.

*Application.*—Wool scarlet R is dyed on wool in the same way as Xylidine scarlet and the other acid dyestuffs; it yields a fiery scarlet, which is fairly fast to light and to washing, acids, and alkalies.

#### BUFFALO RUBIN (Schoellkopf). AZO-BORDEAUX (Bayer).

Alpha-naphthylamine—(1) naphthol 4:8 disulphonic acid.

Brown powder; aqueous solution, magenta-red; HCl, no change; NaOH, no change; solution in  $H_2SO_4$ , blue; on diluting, magenta-red.

*Application.*—Buffalo rubin is also dyed on wool like Xylidine scarlet. It levels fairly well and dyes a claret-red shade, which is fairly fast to light and washing, acids, and alkalies.

#### FAST RED or FAST RED A or O.

ROCELLIN, RAURACIENNE, CERASIN, ORCELLIN NO. 4, RUBIDIN  
CARDINAL RED.

Naphthionic acid—beta-naphthol.

Brown-red powder, sparingly soluble in cold water; aqueous solution, red; HCl, yellowish-brown precipitate; NaOH, dark purplish-red; solution in  $H_2SO_4$ , violet; on diluting, yellowish-brown precipitate.



*Application.*—Fast red A and the other “Fast reds” have largely replaced orchil in wool and especially in silk dyeing owing to their superior fastness and lower price. Fast red A is chiefly used for full red shades, whereas for mixtures better levelling dyestuffs are preferred. It is now but little used for cotton dyeing. It can be dyed in the same way as the Xylidine scarlets on the various fibres. It is, however, more difficult to dye this colour evenly on wool, since it is too rapidly taken up by the fibre, the methods indicated below are more suitable for dyeing wool with Fast red.

**Cotton.**—Fast red A forms a precipitate with alum; hence cotton which has been mordanted with basic alum must be washed in water before dyeing. The colour is not fast to washing.

Wool is dyed according to the first method (p. 512), the bath being heated gradually to the boil, as the dyestuff does not readily dye level. The fourth and fifth methods given in the introduction of this chapter are also well adapted, especially the fourth method (p. 513). The colour also dyes well in a neutral bath, and may, therefore, serve for shading the wool in union dyeing. Fast red A produces a bright red shade on wool, which, however, is only moderately fast to light; it is fairly fast to washing, and not affected by dilute acids or alkalis.

Silk is dyed in an acidified bath of boiled-off liquor. Make the bath slightly acid with sulphuric acid, add the colour solution, turn the goods for 10 to 15 minutes in the warm bath, heat to the boil and work at this temperature for 20 to 25 minutes, rinse in water, brighten in sulphuric acid, wring, and dry. Fast red is dyed very extensively on silk.

**FAST RED B. BORDEAUX B, B L, G, or R. CERASIN.**

Alpha-naphthylamine—beta-naphthol disulphonic acid (R salt).

Brown powder; aqueous solution, claret-red; HCl, no change; NaOH, soluble red-brown precipitate; solution in  $H_2SO_4$ , blue; on diluting, crimson.

*Application.*—Same as Xylidine scarlets (see p. 523).

Fast red B dyes bluish claret-red shades, bluer and less pure than Fast red A, which are fairly fast to light and washing, and fast to acids and alkalis.

**FAST RED C. AZO-RUBIN A or S, CARMOISIN, ACID AZO-RUBIN, BRILLIANT CARMOISIN O, MARS RED G.**

Naphthionic acid—alpha-naphthol sulphonic acid (NW).

Red-brown powder; aqueous solution, crimson; HCl, dark red precipitate; NaOH, more yellowish; solution in  $H_2SO_4$ , violet; on diluting, crimson.

*Application.*—Same as Xylidine scarlets (see p. 523).

Fast red C produces red shades on wool intermediate between those of Fast red B and Acid magenta; it is used in the production of compound shades as a substitute for the latter dyestuff, since it is faster to light and washing and not sensitive to alkalis or acids.

**FAST RED D. AMARANTH.**

**BORDEAUX S, ACID AZO-RUBIN 2 B, VICTORIA RUBIN, OENANTHININ, WOOL RED EXTRA, NAPHTHOL RED O or C or S, ACID CRIMSON.**

Naphthionic acid—beta-naphthol disulphonic acid (R salt).

Red-brown powder; aqueous solution, crimson; HCl, no change; NaOH, darker; solution in  $H_2SO_4$ , violet; on diluting, crimson.

*Application.*—Same as Xylidine scarlets (see p. 523).

Fast red D dyes a pure bluish-red shade, which comes near to the claret reds or “bordeaux.” It is fairly fast to light and to washing, good to acids and alkalis, and has the advantage over Fast red A that it levels better.

**FAST RED E or S. NAPHTHOL RED EB.**

Naphthionic acid—beta-naphthol sulphonic acid (S).

Red-brown powder; aqueous solution, claret-red; HCl, darker; NaOH, brownish-red; solution in  $H_2SO_4$ , violet; on diluting, red.

*Application and Properties.*—Same as Fast red A. The shade is similar to Fast red A. The colour goes rather more evenly on to the fibre.

**PALATIN RED A (B.A.S.F.). FAST RED PR.**

Alpha-naphthylamine—alpha-naphthol 3 : 6 disulphonic acid R G.

This naphthol disulphonic acid is identical with that of Palatin scarlet A. (See *Palatin scarlet A*, p. 523.)

Brown powder; aqueous solution, red; HCl, little change; NaOH, red-brown; solution in  $H_2SO_4$ , blue; on diluting, red.

*Application.*—Same as Xylidine scarlets.

Palatin red dyes a very bright and pure bluish shade of red, even finer than Fast red D. It is fairly fast to light and washing, and fast to acids, alkalis, and stoving.

**AZO-RED A (Cassella).**

Alpha-naphthylamine—alpha-naphthol disulphonic acid.

Brown powder; aqueous solution, red; HCl, no change; NaOH, more yellowish; solution in  $H_2SO_4$ , blue; on diluting, at first violet, then red.

*Application.*—Same as Xylidine scarlets. Azo-red A resembles Palatin red and dyes a pure, bright bluish-red, which is fairly fast to light and washing, and fast to acids, alkalis, and stoving. In union dyeing it is used for shading the wool in a neutral bath.

**ARCHIL SUBSTITUTE V (Poirrier, Holliday). NAPHTHION RED.**

Paranitraniline—naphthionic acid.

Brown paste; aqueous solution, red-brown; HCl, brown-red precipitate; NaOH, soluble brown-red precipitate; solution in  $H_2SO_4$ , crimson; on diluting, brown-red precipitate.

*Application.*—The various brands of archil substitutes are intended, as indicated by their names, as substitutes for archil, and produce shades similar to those obtained with archil in an acid bath. They are employed for the production of mixed shades in wool and silk dyeing, and are applied like the other acid levelling colours (pp. 513 and 515). The shades are only moderately fast, and the dyestuffs, therefore, have been replaced to a great extent by the more recent levelling products, such as Azo-grenadin, Azo-fuchsin, Azo-acid magenta, Azo-carmin, Lanafuchsin, &c.

**ARCHIL SUBSTITUTE 3 VN (Poirrier). ARCHIL SUBSTITUTE V (Berlin).**

Paranitraniline—alpha-naphthylamine sulphonic acid (L).

Dark brown powder; aqueous solution, red; HCl, more bluish; NaOH, brownish; solution in  $H_2SO_4$ , red; on diluting, little change.

*Application.*—Same as Archil substitute V.

**ARCHIL SUBSTITUTE N (Cassella). APOLLO RED (Geigy).**

Paranitraniline—alpha-naphthylamine disulphonic acid D.

Brown powder; aqueous solution, brown-red; HCl, crimson; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , crimson; on diluting, no change.

*Application.*—Same as Archil substitute V.

**ORSEILLIN 2 B (Bayer).**

Aminoazotoluene monosulphonic acid—alpha-naphthol sulphonic acid (N W).

Brown powder; aqueous solution, crimson; HCl, red-violet; NaOH, more yellowish; solution in  $H_2SO_4$ , blue; on diluting, crimson.

*Application.*—Orseillin 2 B is dyed like Fast red A on wool and silk, and yields a yellowish-claret shade, fairly fast to light and milling, and good to acids and alkalis.

**BORDEAUX B X (Bayer).**

Aminoazoxylene disulphonic acid—beta-naphthol.

Brown powder; aqueous solution, brown-red; HCl, brown-red precipitate; NaOH, soluble brown-red precipitate; solution in  $H_2SO_4$ , green; on diluting, brown-red precipitate.

*Application.*—Same as Orseillin B B.

Bordeaux B X dyes more bluish shades of claret-red of similar properties.

**BRILLIANT ARCHIL C (Cassella).**

Azide, produced by the action of nitrous acid on the azo-dyestuff from diazotised *p* nitraniline and 1 : 8 naphthylene diamine 3 : 6 disulphonic acid.

Brown-red powder; aqueous solution, magenta-red; HCl, crimson-red; NaOH, blue; solution in  $H_2SO_4$ , blue; on diluting, violet-red.

*Application.*—Brilliant archil C in an acid bath levels very well on wool and silk, and yields a bright bluish-red, moderately fast to light, fairly fast to washing, and good to acids, alkalis, and stoving.

**CHROMAZON RED (Geigy).**

Aminobenzaldehyde—dioxynaphthalene sulphonic acid.

Brown-red powder; aqueous solution, red; HCl, paler; NaOH, crimson; solution in  $H_2SO_4$ , blue; on diluting, red.

*Application.*—Chromazon red in an acid bath levels very well on wool and silk. It possesses great tinctorial power, and dyes a very brilliant red, brighter than the majority of the azo-colours. It is moderately fast to light and washing and good to acids and alkalis.

**AZO-GRENADIN L and S (Bayer).**

Azo-grenadin L : *p* amidoacetanilide—1 naphthol 4 sulphonic acid.

Azo-grenadin S : *p* amidoacetanilide—1 naphthol 3 : 6 disulphonic acid.

Brown powder; aqueous solution, magenta-red; HCl, little change; NaOH, orange-red; solution in  $H_2SO_4$ , red; on diluting, red.

*Application.*—According to method I. (pp. 513 and 515), Azo-grenadin is dyed on wool in a boiling acid bath and on silk in a hot acid bath with or without boiled-off liquor. Both brands level well, and yield fairly bright red shades of good fastness to acids, alkalis, and stoving, and fairly good fastness to light and washing.

**LANAFUCHSIN S G and S B (Cassella).**

Brown powder; aqueous solution, orange-red (S G) or bluish-red (S B); HCl, little change; NaOH, makes the solution more yellowish; solution in  $H_2SO_4$ , red; on diluting, red.

*Application.*—According to method I. (pp. 513 and 515), Lanafuchsin yields on wool and silk fairly bright shades from yellowish-red to bluish-red of fairly good fastness to light and washing, and good fastness to acids, alkalis, and stoving. Both brands level well, and are very useful for the production of mixed shades on yarns and piece goods.

**LANAFUCHSIN 6 B (Cassella)** dyes magenta-red shades of similar properties.

**SORBIN RED** (B.A.S.F.); **AMIDONAPHTHOL RED G, 2 B, 6 B** (M.L.B.); **AZO-ACID MAGENTA G and B** (M.L.B.); **AZO-ACID CARMINE B** (M.L.B.); **GUINEA RED 4 R** (Berlin); **ERIO RUBIN G, 2 R** (Geigy); **ERIO CARMINE R** (Geigy); **BRILLIANT ACID CARMINE G, B, 6 B** (Griesheim-Oehler); **FLORIDA RED G, B** (Leonhardt) are similar to the preceding dyestuffs, all being azo-reds of very satisfactory fastness, which dye level.

**TOLAN RED B** (Kalle).

Aniline—1 : 8 aminonaphthol 4 : 6 disulphonic acid K.

Brown powder; aqueous solution, magenta-red; HCl, soluble yellowish-brown precipitate; NaOH, orange-red; solution in  $H_2SO_4$ , magenta-red; on diluting, yellowish-brown.

*Application and Properties.*—Similar to the preceding dyestuffs. Tolan red is chiefly used for wool. It also belongs to the well levelling azo-reds, and yields bluish-reds of very satisfactory fastness.

**TOLAN RED G** (Kalle) is similar, and dyes more yellowish shades of red.

**AZO-CORALLIN** (Dahl).

Aminoacetanilide—beta-naphthol disulphonic acid (R salt).

Cinnamon-red powder; aqueous solution, orange-red; HCl, little change; NaOH, more yellowish; solution in  $H_2SO_4$ , yellowish-red; on diluting, orange-red.

*Application.*—Azo-corallin dyes on wool in a boiling acid bath level yellowish-reds of fairly good fastness to light and washing, and good fastness to acids, alkalies, and stoving.

**AZO-FUCHSINE** (Bayer).

A number of brands—*e.g.*, Azo-fuchsine B, G, G N, S—are in the market.

Azo-fuchsine "B" is the azo-compound of toluidine, and "G" that of sulph-anilic acid with 1 : 8 dioxynaphthalene 4 sulphonic acid. The various brands show similar reactions.

Brown powder; aqueous solution, magenta-red; HCl, more yellowish (G) or soluble precipitate; NaOH, more yellowish (G N) or little change; solution in  $H_2SO_4$ , cherry-red (G N) or violet; on diluting, magenta-red.

*Application.*—Like the preceding dyestuffs. The Azo-fuchsines are also well levelling azo-reds which approach Acid magenta in brightness of shade, being fairly fast to light, washing, and alkalies, and fast to acids. Azo-fuchsine B, the most bluish brand, is still yellower than Acid magenta. Azo-fuchsine S possesses the best fastness to alkalies.

Aluminium and chromium salts change the shade to black. This property may be made use of for dyeing worsted piece goods containing silk checks. Azo-fuchsine hardly staining silk in a strongly boiling bath, it may serve for colouring the wool at first red, and by subsequent chroming black, the silk remaining colourless or being dyed to any desired shade in a second bath.

**AZO-FUCHSINE 6 B** (Bayer) is similar to the preceding brands, but dyes much more bluish and also purer shades of red.

**FAST ACID MAGENTA** (Bayer).

Aniline—1 : 8 aminonaphthol 3 : 6 disulphonic acid H.

Brown powder; aqueous solution, magenta-red; HCl, soluble red precipitate; NaOH, orange-red solution; solution in  $H_2SO_4$ , magenta-red; on diluting, red.

*Application.*—Fast acid magenta dyes on wool in a boiling acid bath a fairly bright bluish-red, but yellower and duller than Acid magenta. It levels well and is fast to acids and alkalies and to stoving, and fairly fast to washing, but changes on exposure to light within a short time to dull violet.

**BRILLIANT BORDEAUX S (Berlin).**

Alpha-naphthylamine—1 naphthol 3 : 8 disulphonic acid a.

Red powder; aqueous solution, magenta-red; HCl, slightly bluer; NaOH, darker; solution in  $H_2SO_4$ , blue; on diluting, at first violet, then red.

*Application.*—Brilliant bordeaux S is dyed on wool in a boiling acid bath, and on silk in acidulated boiled-off liquor. It levels well and yields fairly bright red shades of fairly good fastness to light and washing, and good fastness to acids, alkalies, and stoving.

**ORCHIL RED A (B.A.S.F.). UNION FAST CLARET (Levinstein).**

Aminoazoxylene—beta-naphthol disulphonic acid (R salt).

Dark brown powder; aqueous solution, dark bluish-red; HCl, brown-red precipitate; NaOH, soluble brown-red precipitate; solution in  $H_2SO_4$ , dark blue; on diluting, crimson.

*Application.*—Same as Fast red A. Orchil red A dyes on wool in an acid bath a valuable shade of bluish-red, which is distinguished by very good fastness to light and washing, acids and alkalies.

The dyestuff can also be dyed (like the Cloth reds) on wool which has been previously mordanted with chromium, and thus yields more brownish shades, which resemble the Cloth reds in fastness to milling (see under *Mordant Colours*).

**MILLING RED G (Cassella).**

Light brown powder; aqueous solution, orange-red; HCl, soluble brown precipitate; NaOH, little change; solution in  $H_2SO_4$ , red-violet; on diluting, at first orange-red, then brown precipitate.

*Application.*—Milling red G is dyed on wool with the addition of acetic acid and sodium sulphate (Method IV., p. 513), and yields yellowish-reds of very good fastness to milling, acids, and alkalies, which are moderately fast to light. The fastness to milling is improved by a treatment with chromium fluoride in the exhausted dye-bath.

**WOOL RED B (Cassella).**

Brown powder; aqueous solution, bluish-red; HCl, no change; NaOH, soluble violet-red precipitate; solution in  $H_2SO_4$ , violet in transmitted, blue in reflected light; on diluting, at first blue, then red.

*Application.*—Wool red B is dyed in an acid bath on wool and silk, and yields good claret shades of excellent fastness to light, washing and milling, acids, and alkalies. The fastness to milling is further improved by treatment with bichromate in the exhausted dye-bath, and by dyeing Wool red on chromed wool. The dyestuff also dyes fairly well in a neutral bath, and may be used for shading wool in union goods dyed by the one-bath method.

**WOOL RED G and R (B.A.S.F.).**

Brown powder; aqueous solution, red; HCl, brown precipitate; NaOH, dark red; solution in  $H_2SO_4$ , violet; on diluting, brown precipitate.

*Application.*—Wool is dyed in an acid bath with the addition of acetic or sulphuric acid. Wool red G dyes a scarlet-red, Wool red R a more bluish-red of very good fastness to milling and washing, acids, and alkalies, and fairly good fastness to light. Wool red works also well in a neutral bath, or may be dyed together with mordant colours or acid chrome colours.

**CHROMOTROPE 2 R, 2 B, 6 B, 8 B, 10 B (M.L.B.).**

These brands of Chromotrope are azo-compounds of the so-called Chromotrop acid—(1 : 8) dioxynaphthalene (3 : 6) sulphonic acid, with diazotised aniline (2 R), or *p* nitraniline (2 B), or *p* amidoacetanilide (6 B), or naphthionic acid (8 B), or alphanaphthylamine (10 B) respectively. They are dark

coloured powders, which freely dissolve in water with a red to red-violet colour; HCl, little change; NaOH, slightly darker or more bluish; solution in  $H_2SO_4$ , bluish-red (2 R), or red-violet (2 B and 6 B), or blue (8 B and 10 B); on diluting, red to violet.

*Application.*—The Chromotropes are almost exclusively used for wool-dyeing. They may be used either direct or after-treated, all the Chromotropes being converted into blues or blacks by treatment with metallic salts, such as aluminium-, copper-, chromium-salts, and bichromates.

The more yellowish brands, Chromotrope 2 R and 2 B, and also the two brands, Azo acid magenta G and R (p. 531), which are nearly related to them, level very well, and are principally used for mixed shades on piece goods according to Method I., p. 513. Chromotrope 2 R dyes a brilliant scarlet, the brand 2 B a yellowish-red, and Chromotrope 6 B, which levels fairly well, a more bluish-red. The shades are very fast to light, acids, and stoving, and moderately fast to washing; 2 R is fairly fast to alkalis. 2 B thereby is turned violet.

Chromotrope 8 B and 10 B dye magenta-red shades of equal fastness. These two brands, however, are most generally used for black dyeing by afterchroming with 3 per cent. bichrome in the exhausted dye-bath during three-quarters to one hour. These blacks are very fast to light, acids, and stoving, but not to milling, and are more or less affected by alkalis.

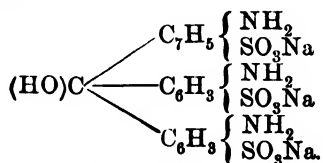
#### CHROMOTROPE F B and S (M.L.B.)

These two dyestuffs are similar to the preceding brands. Chromotrope F B shows the reactions of Fast red C.

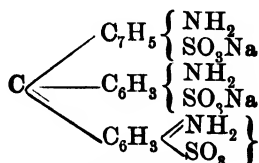
Brown powder; aqueous solution, crimson: HCl, dark red precipitate; NaOH, more yellowish (F B) or darker (S); solution in  $H_2SO_4$ , violet (F B) or blue (S); on diluting, crimson.

*Application.*—These two brands are chiefly used for black and navy blue, fast to wearing on woollen and worsted piece goods. When dyed without chroming, Chromotrope F B dyes a full red, and S a claret shade. The bath is prepared with 10 per cent. Glaubersalt, 4 per cent. sulphuric acid, and 4 to 6 per cent. dyestuff, and, after entering the goods at  $50^\circ$  to  $60^\circ$  C., it is heated within half an hour to boiling, and boiled for about one hour. After this it is cooled off,  $1\frac{1}{2}$  to 2 per cent. bichrome and 1 per cent. sulphuric acid are added, and the colour developed by boiling one hour. Chromotrope F B dyes a dark navy blue, which may be brightened by an addition of Patent blue V or A; the brand S dyes black. The shades are very fast to light, washing, acids, alkalis, and rubbing, and fairly fast to milling. The fastness to milling is improved by an addition of 3 to 4 per cent. lactic acid (50 per cent.) with the bichrome, of which as much as of dyestuff is to be used in this case, the quantities of sulphuric acid also being increased by 1 to 2 per cent. each time.

ACID MAGENTA. ACID FUCHSINE; ACID RUBINE; FUCHSINE S; RUBINE S.



Neutral colourless salt.



Acid-coloured salt.

Acid magenta is obtained by the action of fuming sulphuric acid on Magenta; it consists of mixtures of the trisulphonic acids of Rosaniline and Pararosoniline in the form of their sodium or ammonium salts (see *Magenta*). The normal salt is colourless, whereas the acid salts, as represented by the

above formula, and the acid in the free state are coloured. The colourless salt is constituted analogously to the colourless Rosaniline-base, and contains the carbinol group  $\text{OR}_2\text{OH}$ ; the coloured compounds have probably a constitution corresponding to the coloured salts of Magenta, &c., containing no carbinol group, but the double quinone-binding (see *Magenta*). The same constitution may be ascribed to the colour on the fibre.

The commercial article is sold in the form of the acid salt, since the normal salt is hygroscopic. The aqueous solution of Acid magenta is decolourised on addition of caustic alkalis; the red colour is restored by carbonic acid. Reducing agents transform Acid magenta into leucaniline trisulphonic acid, which yields on oxidation the original Acid magenta.

Dark green crystalline powder, with a metallic reflex, or dark red powder, aqueous solution, crimson; HCl, no change; NaOH, decolourises the solution almost completely; solution in  $\text{H}_2\text{SO}_4$ , yellow; on diluting, crimson.

The presence of ordinary Magenta in Acid magenta can be shown by adding some ammonia and ether to the solution of the dyestuff; ordinary Magenta colours the ether yellowish, and the ether when added to acetic acid colours the latter red; pure Acid magenta colours neither the ether nor the acetic acid (*Kertess*).

*Application*.—Acid magenta cannot be dyed on cotton or linen. It is used in great quantities for the dyeing of wool and silk, principally for the production of compound shades. The shade is similar to ordinary Magenta.

Wool is dyed, according to Method I. (p. 513), with the addition of 2 to 4 per cent. of sulphuric acid or sodium bisulphate and 10 to 20 per cent. of Glaubersalt.

Acid magenta dyes very level. It is not fast to light, but moderately fast to milling, and does not rub. It is, however, decolourised by the action of alkalis (the colour being restored by acids), hence it is not well adapted for goods that have to be milled, or those which should resist alkaline street dirt.

Silk is dyed in a bath of boiled-off liquor that has been slightly acidified with sulphuric acid, or in a slightly acidified bath without boiled-off liquor. Add the colour solution gradually, then heat to about  $90^\circ\text{C}$ ., and continue at this temperature for fifteen to twenty minutes, wash and brighten with sulphuric or tartaric acid, wring, and dry.

**IMPURE ACID MAGENTAS; GRENAT S; MAROON S** are analogous to the impure ordinary magentas, and are applied in the same way as the Acid magenta S.

**FAST ACID EOSIN G (M.L.B.).**

This dyestuff seems to belong to the group of sulphonated Rhodamines.

Fiery vermilion-red powder; aqueous solution, yellowish-red with a very strong green fluorescence; HCl, yellowish-red precipitate, soluble with a yellowish-red colour and very strong fluorescence; NaOH, dark red with a very strong dark olive-green fluorescence; solution in  $\text{H}_2\text{SO}_4$ , yellow with a weak green fluorescence; on diluting, at first reddish-yellow, then pink with a green fluorescence.

*Application*.—Fast acid eosin is dyed on wool by Method I. (p. 513). It levels well, but does not exhaust very well, and, therefore, it is chiefly adapted for pale shades lying between salmon-red and pink. The shades are fairly fast to light, washing, and alkalis, and good to acids and stoving.

**FAST ACID PHLOXIN A (M.L.B.)** is similar to Fast acid eosin G, but dyes more bluish shades of pink and red.

**ACID RHODAMINE R, R R, S R (B.A.S.F., Ch. Ind. Basle).**

Red powder; aqueous solution, red with a yellow fluorescence; HCl, little change; NaOH, little change; solution in  $\text{H}_2\text{SO}_4$ , yellow; on diluting, red.

*Application*.—The Acid rhodamines are dyed on wool in acid baths, and

dye very brilliant reds of relatively good fastness to light. Acid rhodamine R dyes a yellowish Eosin-like shade and 3 R resembles Rhodamine B in shade, whilst Acid rhodamine R R is intermediate.

**AZO-CARMINE (B.A.S.F.).**

Sodium disulphonate of phenylrosinduline.

Phenylrosinduline, the mother-substance of this dyestuff, is produced by heating *anilidonaphthoquinoneanile* with aniline and aniline hydrochloride to 130° or 160°. Azo-carmines are prepared from this compound with the aid of fuming sulphuric acid. Azo-carmines G in paste, the more yellowish brand, is the disulphonate, and Azo-carmines B is the trisulphonate.

*Azo-carmines G.*—Red paste with a bronze lustre; sparingly soluble in water; aqueous solution, crimson; HCl, red precipitate; NaOH, no change; solution in H<sub>2</sub>SO<sub>4</sub>, green; on diluting, crimson solution and crimson precipitate.

*Azo-carmines B* is a red-violet powder, readily soluble in water, which shows fairly the same reactions as the "G" brand (see also *Rosinduline*).

*Application.*—Azo-carmines B levels very well on wool and is dyed by the first method (p. 513). Azo-carmines G levels less well and is dyed by the first or second method (*l.c.*). Both brands dye bluish shades of red, less bluish and less brilliant than Acid magenta. They are fairly fast to light and milling, and not sensitive to dilute acids and alkalis. The dyestuffs are very valuable in wool dyeing for the production of compound shades, and are excellent orchil substitutes.

**ROSINDULINE 2 B, B, G, 2 G (Kalle).**

These dyestuffs closely resemble Azo-carmines in reactions and tinctorial properties. Rosinduline 2 B is said to be identical with Azo-carmines B and possesses the best fastness. Rosinduline 2 G, the most yellowish brand, dyes a fiery orange-red with a strong yellowish fluorescence on silk.

**X L RED (Holliday).**

This dyestuff, according to the maker, has a constitution similar to Azo-carmines.

Brown powder; aqueous solution, crimson; HCl, no change; NaOH, makes the solution paler and more yellowish; solution in H<sub>2</sub>SO<sub>4</sub>, green; on diluting, red.

*Application and Properties.*—Same as Azo-carmines. X L red dyes a very bluish-red or rather violet-red, moderately fast to light, fairly fast to milling, and good to acids and alkalis.

**X L ACID EOSIN 5 B and 3 B (Holliday).**

X L Acid eosin 5 B is an azo-dyestuff, the constitution of which has not been published. The 3 B brand is a mixture with orange.

Brick-red powder; aqueous solution, crimson; HCl, crimson precipitate; NaOH, orange; solution in H<sub>2</sub>SO<sub>4</sub>, bluish-red; on diluting, crimson precipitate.

*Application.*—This dyestuff is dyed on wool in an acid bath and levels well. It dyes scarlet-red shades with a fine blue shine overhand; it is fairly fast to light and alkalis, good to acid and stoving, and moderately fast to washing.

**FAST VIOLET, REDDISH (Bayer).**

Sulphanilic acid—azo-naphthylamine—beta-naphthol sulphonic acid (S).

For the production of this dyestuff sulphanilic acid is diazotised and combined with alphanaphthylamine; the product is rediazotised and combined with alphanaphthol sulphonic acid (S).



Dark powder with a green metallic reflex; aqueous solution, red-violet; HCl, red-violet precipitate; NaOH, soluble red-violet precipitate; solution in  $H_2SO_4$ , dark bluish-green; on diluting, red-violet precipitate.

*Application.*—Fast violet dyes in an acid bath dull reddish-violet to violet-black shades on wool, which are fairly fast to light and to washing; it is applied in the same way as the other acid colours. On wool which has been mordanted with chromium oxide Fast violet produces darker shades.

#### FAST VIOLET, BLUISH (Bayer).

Paratoluidine sulphonic acid—azo-naphthylamine—  
beta-naphthol sulphonic acid (S).

This colouring matter is produced analogously with the preceding one.

Dark brown powder; aqueous solution, violet; HCl, violet precipitate; NaOH, soluble violet precipitate; solution in  $H_2SO_4$ , dark green; on diluting, violet precipitate.

*Application and Properties.*—Same as Fast violet, reddish. The shade is a dull violet.

#### AZO ACID VIOLET 4 R, R, and B (Bayer).

Azo-dyestuffs which, by their constitution, are related to the Azo-fuchsines.

*Azo-Acid Violet 4 R.*—Dark brown powder; aqueous solution, red; HCl, bluer solution; NaOH, soluble orange-red precipitate; solution in  $H_2SO_4$ , violet-red; on diluting, same.

*Application.*—Azo-acid violet, like the Azo-fuchsines, dyes very level on wool in an acid bath, and yields red-violets of moderate brightness, which are moderately fast to light, and fairly fast to washing, acids, and stoving; alkalis turn the shades light-red.

#### VICTORIA VIOLET 5 B (Bayer).

Black powder; aqueous solution, violet; HCl, soluble violet precipitate; NaOH, brown-red solution; solution in  $H_2SO_4$ , violet; on diluting, violet-red.

*Application.*—This azo-dyestuff also levels well on wool in an acid bath and dyes a not very bright bluish-violet, fairly fast to light, washing, and acids, but reddened by alkalis.

#### VICTORIA VIOLET 4 B S and 8 B S (M.L.B.)

*Victoria Violet 4 B S* is the sodium salt of *p* aminobenzene-azo (1:8) dioxynaphthalene (3:6) disulphonic acid and is produced by alkaline reduction of Chromotrope 2 B or by splitting off the acetyl-group from Chromotrope 6 B (p. 532).

*Victoria Violet 8 B S* and Azo-acid blue B (p. 543) belong to the same class of dyestuffs and show similar reactions.

Brown-black powder; aqueous solution, violet; HCl, red solution, NaOH, orange-red solution; solution in  $H_2SO_4$ , red-violet; on diluting, yellowish-red.

*Application.*—These dyestuffs level very well on wool in acid baths. *Victoria violet 4 B S* dyes a not very bright bluish-violet and *8 B S* a brighter and more bluish-violet, which are moderately fast to light, and fairly fast to washing; mineral acids and alkalis slightly redden the shades; hence the colours come out more bluish if the sulphuric acid in dyeing is replaced by alum.

#### AZO-WOOL VIOLET 7 R (Cassella).

Brown powder; aqueous solution, violet-red; HCl, little alteration of the solution and formation of a soluble precipitate; NaOH, little change; solution in  $H_2SO_4$ , violet-red; on diluting, little change.

*Application.*—Azo-wool violet 7 R also levels very well on wool in an acid bath and dyes a violet not very bright in shade, but rather good in fastness to light, fairly fast to washing, and fast to acids, alkalis, and stoving. The dye-stuff serves well for violets, clarets, prunes, and blues on yarns and piece goods.

**LANACYL VIOLET B** (Cassella).(1 : 8) Aminonaphthol (3 : 6) disulphonic acid H—ethyl  $\alpha$ -naphthylamine.

Dark brown powder; aqueous solution, red-violet; HCl, no change; NaOH, orange-red; solution in  $H_2SO_4$ , greenish-blue; on diluting, at first blue, then violet.

*Application and Properties.*—Same as Lanacyl blue B B (p. 543). Lanacyl violet B dyes a not very bright bluish-violet, which is very good in fastness to light, washing, acids, and alkalies.

**BIEBRICH ACID VIOLET 2 B and 6 B** (Kalle).

Azo-dyestuffs with (1 : 8) dioxynaphthalene (4 : 6) disulphonic acid K.

*Biebrich Acid Violet 2 B.*—Black-brown powder; aqueous solution, red-violet; HCl, soluble brown precipitate; NaOH, orange-red; solution in  $H_2SO_4$ , red-violet; on diluting, red.

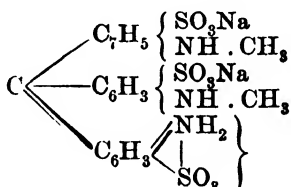
*Application.*—Biebrich acid violet belongs to the group of azo-dyestuffs well levelling on wool in acid baths and possesses fairly good fastness to light, washing, acids and alkalies. The brand 2 B dyes a medium violet and 6 B a bluish-violet which resemble the other azo-violets in brightness.

**FAST SULPHONE VIOLET 5 B S** (Sandoz).

Brown powder; aqueous solution, violet; HCl, brick-red precipitate; NaOH, brown-red; solution in  $H_2SO_4$ , red; on diluting, brick-red precipitate.

*Application.*—Fast sulphone violet 5 BS is dyed on wool and silk in acid baths. It levels fairly well and yields a not very bright bluish-violet, which possesses fairly good fastness to light, washing, acids, alkalies, and stoving.

**FAST SULPHONE VIOLET 4 R** (Sandoz) and **BRILLIANT SULPHONE RED B** (Sandoz) are similar dyestuffs, which dye red-violet or red shades respectively, in fastness to acids and alkalies they are superior to the preceding brand.

**RED-VIOLET 4 RS** (B.A.S.F.). **ACID VIOLET 4 RS.**

Red-violet 4 RS is prepared by the action of fuming sulphuric acid on dimethylrosaniline, and is the sodium trisulphonate of this base.

Red-violet powder; aqueous solution, crimson; HCl, no change; NaOH, light reddish-yellow; solution in  $H_2SO_4$ , brown-yellow; on diluting, crimson.

*Application and Properties.*—Same as Acid magenta. Red-violet 4 RS dyes a bluish shade of red, a little more bluish than Acid magenta. The shade is moderately fast to light and milling, but very sensitive to soda, ammonia, or alkaline road dirt.

Red-violet 4 RS and 5 RS can also be dyed on chromium mordant; this property is common to the various Acid violets.

**RED-VIOLET 5 RS** (B.A.S.F.).

Red-violet 5 RS is the sodium trisulphonate of monoethylrosaniline, prepared analogously to Red-violet 4 RS.

Brown-violet lumps with a metallic reflex; aqueous solution, crimson; HCl, no change; NaOH, light brown-yellow; solution in  $H_2SO_4$ , yellow; on diluting, crimson.

*Application and Properties.*—Same as Red-violet 4 RS; the shade is slightly more bluish.

**ACID VIOLET 2 B (B.A.S.F.).**

This product is the sodium salt of the sulphonic acid of ordinary Methyl violet, and is produced by the action of sulphuric acid on this colouring matter.

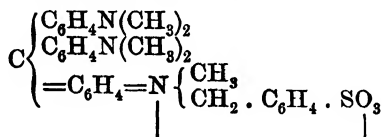
*Application and Properties.*—Acid violet 2 B is similar to Red-violet 4 R S, but dyes a bluer shade of violet than this colouring matter.

**ACID VIOLET.**

Under this denomination a number of similar dyestuffs are furnished by most colour makers, which all dye wool and silk violet in an acid bath. They are dyed on wool in boiling acid baths according to method I. (p. 513), and level very well. They are slightly faster to light than the preceding Red-violets, and much better in fastness to alkalis, so as to resist carbonate of soda, ammonia, and alkaline street dirt; in addition they are fairly fast to washing, milling, acids, and stoving. These Acid violets find their principal application for the dyeing of bright violets, blues, &c., on woollen piece goods, yarns, and shoddy, and are used together with Acid green, Acid magenta, Orange II., Naphthol yellow S, &c., for dyes which are not required to be very fast. They also dye well in a feebly acid bath, and are, therefore, used for shading logwood and other colours on chromed wool in a bath acidulated with acetic acid; or they may be dyed by the one-bath method, together with logwood, ferrous sulphate, and cupric sulphate. Since they generally withstand chromic acid they are also dyed together with the acid chrome colours for brightening them.

The various Acid violets of this kind are brought into the market in the form of brands marked from 2 B to 12 B, of which the bluish-violet brands 4 B to 7 B probably are those most frequently used. They resemble each other both by their chemical constitution, their reactions, and their tinctorial properties; we, therefore, refrain from registering each brand, but will name only those the constitution of which has been published.

**ACID VIOLET 4 B N (B.A.S.F., Chem. Ind. Basle).** **ACID VIOLET 6 B (Bayer).** **ACID VIOLET N (M.L.B.).** **ACID VIOLET 7 B (Leonhardt).**



This product is obtained by the sulphonation of benzylpentamethylparosaniline (prepared by the condensation of tetramethyldiaminobenzophenone chloride and benzylmethylaniline), or by the sulphonation and subsequent oxidation of the leuco-compound of the above-named base.

Violet-brown powder; aqueous solution, blue-violet; HCl, blue precipitate, which dissolves in excess with an olive colour, the solution becomes on diluting with water first green and then blue; NaOH, blue precipitate; on heating, colourless solution; solution in H<sub>2</sub>SO<sub>4</sub>, brownish-orange; on diluting, at first olive, then green, at last blue.

*Application and Properties.*—Same as Acid violet (see above). *Acid violet 4 B N* dyes a bluish-violet shade.

**ACID VIOLET 6 B N (B.A.S.F., Ch. Ind. Basle).**

This dyestuff, similar to the brand 4 B N, is prepared by sulphonating the compound obtained by condensation of tetramethyldiaminobenzophenone chloride with *m* ethoxyphenyltolylamine.

Acid violet 6 B N is a blue-violet powder, giving with H<sub>2</sub>SO<sub>4</sub> a brownish-yellow solution, and otherwise showing the same reactions as 4 B N.

*Application and Properties.*—Same as Acid violet (see above). The shade is that of a fairly bluish-violet.

**ACID VIOLET 6 B (Berlin).**

Acid violet 6 B is prepared by the oxidation of the leuco-compound which is obtained by condensation of dimethylpara-aminobenzaldehyde and ethylbenzylaniline sulphonic acid.

Blue-violet powder; aqueous solution, violet; HCl, bluish-green; NaOH, decolourises; diluted solutions are light blue; solution in  $H_2SO_4$ , yellowish-brown; on diluting, from dark brown to bluish-green.

*Application and Properties.*—Same as Acid violet (p. 538).

Acid violet 6 B dyes a fairly bluish-violet, moderately fast to alkalis.

**ACID VIOLET 7 B (B.A.S.F., Ch. Ind. Basle).**

Acid violet 7 B is produced by the action of diethylaminobenzoyl chloride upon methyldiphenylamine and subsequent sulphonation.

Violet powder; aqueous solution, violet-blue; HCl, green; NaOH, violet precipitate in the cold, colourless solution on warming; solution in  $H_2SO_4$ , orange-brown; on diluting, at first dark olive-green, finally bluish-green.

*Application and Properties.*—Same as Acid violet (p. 538). The brand 7 B dyes a pure bluish-violet, slightly bluer than 6 B N, and moderately fast to alkalis.

**GUINEA VIOLET 4 B (Berlin)** also belongs to this group, and is superior to the preceding Acid violet 6 B in fastness to alkalis.

**ACID VIOLET 7 B N (M.L.B.).**

This dyestuff is obtained by condensing tetramethyldiaminobenzhydrol sulphonic acid with dibenzylaniline sulphonic acid.

Blue-violet powder; aqueous solution, blue; HCl, green; NaOH, decolourised on heating; solution in  $H_2SO_4$ , orange-yellow; on diluting, blue.

*Application and Properties.*—Same as Acid violet (p. 538). The shade is that of a bluish-violet.

**ACID VIOLET 5 B N S, 6 B N S, 7 B S (Sandoz).**

These dyestuffs are produced by condensation of tetra-alkyldiaminobenzophenone with alkylated or acylated beta-naphthylamine, and subsequent sulphonation.

Dark violet powder; aqueous solution, violet; HCl, violet precipitate, dissolving in excess to a green to yellowish-brown solution; NaOH, blue solution, lighter on warming; solution in  $H_2SO_4$ , yellowish-brown; on diluting, at first green, then blue.

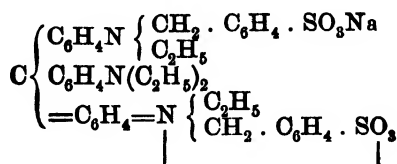
*Application and Properties.*—Same as Acid violet (p. 538). These dyestuffs dye more or less bluish-violets of rather good fastness to alkalis.

**FAST ACID VIOLET 10 B (Bayer).**

This dyestuff is produced by condensation of tetramethyldiaminobenzhydrol with ethylbenzylaniline disulphonic acid, and subsequent oxidation.

Brown powder; aqueous solution, reddish-blue; HCl, green solution, with an excess yellow; NaOH, in the cold no change, pink on heating; solution in  $H_2SO_4$ , brown; on diluting with much water, green.

*Application and Properties.*—Same as Acid violet (p. 538). Fast acid violet dyes a pure, very bluish-violet, which resembles the better class of Acid violets in fastness to light, milling, washing, and acids, and possesses good fastness to alkalis. The shade is moderately fast to light, like the other Acid violets.

**FORMYL VIOLET S 4 B (Cassella).**

Formyl violet S 4 B is produced by oxidising together diethyldibenzyl-diaminodiphenylmethane disulphonic acid and diethylaniline. Similar more bluish brands are *Formyl violet S 5 B, 6 B, 8 B, 10 B.*

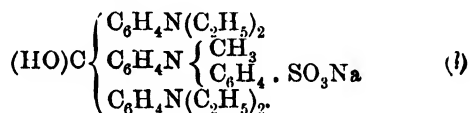
Red-violet powder with a bronze reflex; aqueous solution, violet; HCl, yellow, almost decolourised; NaOH, solution in H<sub>2</sub>SO<sub>4</sub>, orange-yellow; on diluting, yellow to colourless.

*Application.*—Formyl violet is dyed on wool by the first, or better, by the fourth method (p. 513), the bath being heated gradually to the boil, as the dyestuff does not readily dye level. It may also be dyed in a neutral bath, and is very useful for shading the wool in dyeing unions by the one-bath method. It can also be dyed on chromium mordants, or in combination with acid-chrome colours.

Formyl violet S 4 B dyes a full bluish shade of violet, which resembles the better kinds of Acid violets as regards fastness to light, washing, and acids; it is good to alkalies (road dirt), and very fast to milling.

Formyl violet is dyed on silk in boiled-off liquor broken with sulphuric acid, and possesses good fastness to washing and water, which is still improved by a subsequent treatment with tannin and antimony (p. 191).

ALKALI VIOLET 6 B (B.A.S.F.).



Alkali violet is prepared by the sulphonation of methylphenyltetraethyl-pararosaniline (prepared by condensation of tetraethyldiaminobenzophenone and methyldiphenylamine).

Violet powder; aqueous solution, violet; HCl, olive-green; on diluting, blue; NaOH, soluble blue precipitate; on heating, the solution is decolourised; solution in H<sub>2</sub>SO<sub>4</sub>, yellow-brown; on diluting, at first olive, then blue.

*Application.*—Alkali violet can be dyed in an alkaline, neutral, or acid bath, and is applicable to cotton, wool, or silk. It can, therefore, be used for the purpose of reddening Alkali blue, or in conjunction with colours which dye in a neutral bath, or, finally, in an acid bath along with the different colours. It is also useful in dyeing unions by the one-bath method with direct colours for covering or shading the wool. It produces a pure blue-violet shade. More reddish brands are *Alkali violet R* and *4 B.*

Cotton may be dyed with Alkali violet by the usual method employed for the basic colours on a tannin and antimony mordant; the shade is moderately fast to soaping, and a little faster to light than Methyl violet (see pp. 459 and 494).

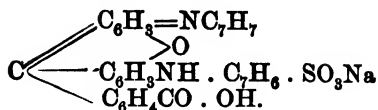
Wool is dyed best in a boiling bath by the same methods as Alkali blue, or in a neutral bath like the Methyl violets.

In an acid bath Alkali violet is dyed on wool according to the requirements of the acid colours with which it is combined; in this case it should, to avoid unevenness, not be dyed very rapidly. Alkali violet on wool is very fast to milling and acids, fairly fast to alkalies, and moderately fast to light.

Silk is dyed with Alkali violet in a boiled-off liquor bath, slightly acidulated with sulphuric acid. Add the colour solution, enter the silk, heat to the boiling point, and work at this temperature for half an hour, wash, brighten in sulphuric acid, wash, and dry. The shade is fast to water and soap.

Silk can also be dyed with Alkali violet in a neutral bath, or by the method used for Alkali blue.

**VIOLAMINE R**, or **FAST ACID VIOLET A 2 R** (M.L.B.), or **ACID VIOLET 4 R N** (B.A.S.F.).



Violamine R is produced by the action of orthotoluidine on fluorescein chloride, and subsequent sulphonation of the compound. It is the sodium salt of *diorthotolylrhodamine sulphonie acid*, and has probably the constitution shown by the above formula.

Light maroon powder; aqueous solution, red, with an orange fluorescence which disappears on heating and reappears on cooling; HCl, pink precipitate; NaOH, no change; solution in  $\text{H}_2\text{SO}_4$ , orange; on diluting, red precipitate.

*Application*.—Violamine R is dyed on wool according to Method I., p. 513, and on silk according to p. 515. It produces an excellent bluish-red, which is similar to, but bluer than, Rhodamine. It dyes evenly, and is satisfactory regarding fastness to light and washing, while the shade is not affected by dilute alkalis. The dyestuff is much faster to light than the preceding Acid violets, and is, in spite of its high price, extremely valuable for the dyeing of wool and silk, especially for the production of fast fancy shades. It may also be dyed on chromed wool or in combination with acid chrome colours, thus yielding very fast shades. Violamine on silk is fast to water, and also serves well for tin-weighted silk.

**VIOLAMINE B** or **FAST ACID VIOLET B** (M.L.B.).

Violamine B is *diparatolylrhodamine sulphonate of sodium*, and is produced analogously to Violamine R by substituting paratoluidine for orthotoluidine.

Maroon powder; aqueous solution, reddish-violet; HCl, purple precipitate; NaOH, cherry-red; solution in  $\text{H}_2\text{SO}_4$ , red-orange; on diluting, red-violet precipitate.

*Application and Properties*.—Same as Violamine R. The shade is red-violet.

**VIOLAMINE G** or **ACID ROSAMINE A** (M.L.B.).

Violamine G or *dimesidylrhodamine sulphonate of sodium* is also produced like Violamine R, by substituting mesidine for orthotoluidine.

Dark red powder; aqueous solution, yellowish-pink; HCl, dark red precipitate; NaOH, slightly yellower; solution in  $\text{H}_2\text{SO}_4$ , orange-brown; on diluting, red precipitate.

*Application and Properties*.—Same as Violamine R and B. This brand chiefly serves for dyeing fine pinks, especially on silk.

**FAST ACID VIOLET B E**, **R B E**, and **R G E** (M.L.B.) are more recent brands of very similar properties, which are superior in fastness to hot pressing.

**ACID MAUVE B** (Holliday).

This seems to be a dyestuff of the Induline series.

Brown granules; aqueous solution, mauve; HCl, soluble red-violet precipitate; NaOH, dull red-violet; solution in  $\text{H}_2\text{SO}_4$ , dull blue; on diluting, violet.

*Application*.—Acid mauve is dyed on wool by the ordinary methods (p. 512), and yields mauve shades of moderate brightness.

**SULPHONE CYANIN G**, **G R**, **3 R**, **5 R** (Bayer). **COOMASSIE NAVY BLUE G**, **G N**, **2 R N**, **3 R** (Levinstein).

These are secondary disazo-dyestuffs, which correspond, for instance, to the constitution—

Aniline—naphthylamine sulphonie acid (Cleve)

—1 : 8 tolylnaphthylamine sulphonie acid.

**Sulphone Cyanin G.**—Dark brown powder; aqueous solution, reddish blue; HCl, greyish-blue precipitate; NaOH, soluble blue precipitate; solution in  $H_2SO_4$ , blue; on diluting, at first greenish-blue, then blue precipitate.

**Application.**—These azo-dyestuffs are chiefly used for dyeing wool in a feebly acid bath, and are best dyed with the addition of 3 to 5 per cent. of ammonium acetate (commercial solution) and 10 per cent. Glaubersalt; enter lukewarm, heat within half an hour to the boil and boil one hour, exhausting the bath, if necessary, by adding some acetic acid. The bath must not become alkaline, otherwise the colour will be destroyed; acidulating the bath with sufficient acetic acid, without, however, using an excess, and an addition of  $\frac{1}{4}$  to  $\frac{1}{2}$  per cent. bichrome are very useful to prevent degrading of the colour. Steaming at more than  $\frac{1}{2}$  or 1 lb. pressure also deteriorates it.

Sulphone cyanin yields full, fairly bright medium blues and Navy blues; the brand G dyes the most greenish shades, the others are considerably more reddish. The colours are distinguished by excellent fastness to light, washing, milling, acids, alkalis, and stoving, and are very useful for loose wool, yarns, and piece goods which do not require severe steaming. They also serve well in the one-bath method of union-dyeing with direct cotton colours for shading the wool, since they dye very well in a neutral bath. Silk is dyed with the addition of ammonium acetate or in boiled-off liquor acidulated with acetic acid, deep blue shades of very good fastness to light being obtained.

**SULPHONE AZURIN** (Bayer, Berlin, Leonhardt, Levinstein).

Benzidine sulphone disulphonic acid  $\left\{ \begin{array}{l} \text{phenyl beta-naphthylamine} \\ \text{phenyl beta-naphthylamine.} \end{array} \right.$

Dark blue powder; aqueous solution, greenish-blue; HCl, dark blue precipitate; NaOH, soluble blue precipitate; solution in  $H_2SO_4$ , violet; on diluting, black-violet precipitate.

**Application.**—Sulphone azurin is a direct cotton colour, but is chiefly valuable for wool which it dyes much better than cotton. Wool is best dyed in a boiling neutral bath with the addition of 10 per cent. Glaubersalt. Fairly bright medium and dark blue shades are obtained of good fastness to milling, acids, and alkalis, and fairly fast to light. Cotton may be dyed like the direct cotton colours with the addition of 10 per cent. salt, a greenish-blue being thus obtained. The dyestuff is also recommended for dyeing unions by the one-bath method, when the wool will be dyed deeper than the cotton, the latter to be filled up with direct cotton colours.

**BRILLIANT SULPHONE AZURIN R** (Bayer).

Dark blue powder; aqueous solution, blue; HCl, dark blue precipitate; NaOH, soluble blue precipitate; solution in  $H_2SO_4$ , violet-black; on diluting, violet-red precipitate.

**Application and Properties.**—Same as Sulphone azurin D. A similar, but brighter, blue is obtained.

**SULPHONE ACID BLUE R, B, G** (Bayer).

Dark blue powder; aqueous solution, blue-violet or blue; HCl, greenish-blue; NaOH, orange-red; solution in  $H_2SO_4$ , dark green or dark blue; on diluting, blue.

**Application.**—Wool is dyed with the addition of Glaubersalt and acetic acid, the bath being exhausted by the addition of 1 to 2 per cent. sulphuric acid. The dyestuffs resemble the Sulphone cyanins in fastness, with the exception of fastness to milling and washing; they are for this reason chiefly used for piece dyeing.

**AZO-ACID BLUE 4 B** (Bayer).

Greyish-black powder; aqueous solution, blue-violet; HCl, soluble red precipitate; NaOH, orange-red; solution in  $H_2SO_4$ , red-violet; on diluting, red.

*Application.*—This dyestuff is dyed on wool in a moderately acid bath with the addition of Glaubersalt and 1 to 2 per cent. sulphuric acid. Not more acid should be used than required to change the colour of the solution, otherwise the bath will not be well exhausted. The dyestuff levels well and dyes a moderately bright blue of moderate fastness and is chiefly applicable for mixed shades.

#### AZO-ACID BLUE B (M.L.B.).

This dyestuff is nearly related to Victoria violet 4 B S and 8 B S (p. 536).

Dark brown powder; aqueous solution, dull violet; HCl, red; NaOH, brownish-red; solution, in  $H_2SO_4$ , magenta-red; on diluting, red.

*Application and Properties.*—Same as Victoria violet. The dyestuff levels very well on wool and dyes a good blue shade brighter and bluer than Victoria violet 8 B S and of the same fastness.

#### COPPER BLUE B (M.L.B.).

Dark brown powder; aqueous solution, red-violet; HCl, red precipitate; NaOH, slightly redder solution; solution in  $H_2SO_4$ , violet-red; on diluting, red precipitate.

*Application.*—Copper blue is an azo-dyestuff for wool, which, by an after-treatment with copper sulphate, dyes full dark blue shades of good fastness.

The dye-bath is prepared with 20 per cent. Glaubersalt, 2 per cent. sulphuric, or 5 per cent. acetic acid and the dyestuff. Enter at 40° to 50° C., heat gradually to the boil; after one hour's boiling add 3 per cent. copper sulphate and continue boiling for twenty minutes. Tartrazin, Flavazin, Orange II., Fast acid violet, or Patent blue may be added for shading. Copper blue is useful for dark blues on piece goods, yarns, and hosiery. The developed colours possess very good fastness to light and washing, and fairly good fastness to acids and alkalies.

#### CYPRUS BLUE R (Berlin).

Dark brown powder; aqueous solution, violet-red; HCl, red precipitate; NaOH, no change; solution in  $H_2SO_4$ , blue-violet; on diluting, red precipitate.

*Application.*—This azo-dyestuff, like the preceding one is also dyed on wool, and developed to blue by an after-treatment with copper sulphate. The bath is prepared with 10 per cent. Glaubersalt, 5 per cent. acetic acid and the dyestuff, and, after entering the material, is brought to the boil within half an hour and boiled one hour. The after-treatment with copper sulphate takes place in the same bath, or, better, in a fresh one. 2 to 3 per cent. acetic acid and one-third to one-half copper sulphate of the weight of dyestuff used are added and the material entered at 60°; raise gradually to the boil and boil half an hour.

A full reddish-blue is obtained of very good fastness to light and washing, and fairly good fastness to acids and alkalies. For shading, the same dyestuffs as for Copper blue B may be used.

#### LANACYL BLUE and LANACYL NAVY BLUE (Cassella).

Lanacyl blue B B—(1 : 8) aminonaphthol (3 : 6) disulphonic acid H—  
(1 : 5) aminonaphthol.

These dyestuffs closely resemble each other and come into the market as Lanacyl blue B B and R and Lanacyl Navy blue B, 2 B, and 3 B.

Dark powder; aqueous solution, red-violet to blue-violet; HCl, little change; NaOH, orange-red with Lanacyl blue, little redder with Lanacyl navy blue; solution in  $H_2SO_4$ , blue; on diluting, at first blue, then violet.

*Application.*—Wool is dyed in an acid bath prepared with 10 per cent. acetic acid. Enter lukewarm, bring gradually to the boil, and boil one hour; exhaust the bath by adding 5 per cent. acetic acid or with Lanacyl navy blue 5 per cent. sodium bisulphate and continue boiling for twenty minutes. Lanacyl blue R dyes reddish deep blues, B B medium and deep greenish-blues, and the other brands full Navy blues. The Lanacyl blues possess very good



fastness to light, washing, acids, and alkalis, and are moderately fast to milling. The Lanacyl navy blues are fairly fast to light, and in other respects they possess the same fastness.

The dyestuffs serve well for fast shades on piece goods and on knitting yarns and carpet yarns. They also work well in a neutral bath, and, therefore, they are used in union dyeing with direct dyestuffs for filling up the wool.

Silk may be dyed by the ordinary methods (p. 515).

**PERI WOOL BLUE B, B G, G** (Cassella).

*Peri Wool Blue B.*—Dark brown powder; aqueous solution, blue-violet; HCl, bluish-red; NaOH, red-violet; solution in  $H_2SO_4$ , bluish-red; on diluting, little change.

*Application.*—Peri wool blue is only dyed on wool in an acid bath according to method I. (p. 513). The material is entered at  $60^\circ$  into the bath prepared with 30 per cent. Glaubersalt and 4 per cent. sulphuric acid, and the bath is raised within three-quarters of an hour to boiling and boiled for one hour, when 2 per cent. more acid is added and severely boiled for half an hour longer. Severe boiling is important for good levelling. Peri wool blue dyes navy blue shades; the brand B is the most violetish and "G" the most greenish. The colours are very fast to light, washing, acids, and alkalis, and fast enough for light milling; they find their chief application for piece goods and carpet yarns. For shading the Peri wool blues are recommended—Cyanol, Cyanol fast green, Orange G G, and Tartrazin.

**ALKALI BLUE (NICHOLSON'S BLUE. SOLUBLE ANILINE BLUE).**

Alkali blue is obtained by the action of concentrated sulphuric acid on Aniline blue, soluble in spirit, and consists of the *monosulphonates of mono- and diphenylrosaniline (and of mono-, di-, and triphenylpararosaniline)* in the form of their sodium salts. Diphenylrosaniline and triphenylpararosaniline yield the purest blue shades, as is also the case with Aniline blue, soluble in spirit. The brands are indicated according to their shades by letters—e.g., Alkali blue 4 R, 6 B, &c.

Blue powder; sparingly soluble in cold, freely soluble in hot water; aqueous solution, blue; HCl, blue precipitate; NaOH, claret-red; solution in  $H_2SO_4$ , red-brown; on diluting, blue precipitate.

Reducing agents convert Alkali blue into the corresponding leuco-compound.

*Application.*—Alkali blue is not used in cotton dyeing, as it cannot be permanently fixed on the fibre. It used to be dyed in former years to a limited extent on cotton which had been mordanted with tannin or printed on calico with the aid of tannin and chromium; but it is not so employed now, since many more suitable dyestuffs have taken its place (Methylene blue, Victoria blue, &c.).

The dyeing with Alkali blue on wool and silk requires a peculiar mode of operation, the colour acid being insoluble in water. The method of dyeing is based on the fact that Alkali blue is taken up by the fibre from an alkaline bath—hence the name—in the form of a colourless salt, and that the coloured compound can be developed on the fibre with the aid of acid. Hence, for dyeing with Alkali blue two baths are required.

In dyeing with Alkali blue calcareous water should be avoided or purified. The dye-baths are never exhausted and should be used continuously. If a deposit has been formed, the clear liquor may be drawn off for further use; the deposit is dissolved with the aid of a very little soda and added to the clear liquor after filtering.

*Wool—First Method.*—Prepare the dye-bath with 1 to 3 per cent. of soda ash or 5 to 10 per cent. of borax or silicate of soda or some ammonia, and add the required amount of colour (about 2 per cent. for a full shade). For 100 litres of the acid bath or developing bath use about 150 to 200 grms.

of sulphuric acid (for 100 galls,  $1\frac{1}{2}$  to 2 lbs.), and the same quantity of alum or sulphate of zinc may be added.

Introduce the wool into the dye-bath at  $60^{\circ}$ , heat within 20 minutes to  $90^{\circ}$ , and maintain this temperature for about 45 minutes.

In order to match off any given shade, a sample of the material is passed from time to time through the developing bath or through warm dilute acid. When sufficient colouring matter has been taken up the goods are lifted from the dye-bath, wrung out and rinsed in water to remove surface colour; the material has now a dull greyish or pale bluish appearance. Enter the goods at  $60^{\circ}$  to  $70^{\circ}$  into the *developing bath*, where they become blue at once work them for about 15 to 20 minutes, until the shade is fully developed; wash and dry. The developing bath should not be heated above  $80^{\circ}$ , otherwise the blue is less brilliant; the addition of alum or zinc sulphate to the bath tends to increase the fastness to milling, since these salts form insoluble lakes with the dyestuff. An excess of alkali in the dye-bath (for Alkali blue) is to be avoided, since it has a dulling effect on the shade; some brands of Alkali blue do not require the addition of alkali, or a small amount only.

*Second Method.*—Work the wool for one hour in a boiling bath which contains 10 per cent. of the weight of the material of borax, wring out, pass into a separate dye-bath (prepared with the required amount of colour), work until a sample acquires the desired shade in dilute acid, wring out and develop as before.

*Third Method.*—Prepare the dye-bath with 5 per cent. of soap and  $2\frac{1}{2}$  per cent. of borax or silicate of soda, dye and develop as by the first method.

Alkali blue yields fine blue shades, which are superior to the Soluble blues in purity and less reddish. The colour is moderately fast to light and fairly fast to milling, and is not affected by dilute acids; by alkalies and alkaline milling the shade is decolourised, but is restored in an acid bath.

Silk and jute are dyed by the third method indicated for wool.

#### SOLUBLE BLUES.

METHYL BLUE (for Cotton). SOLUBLE BLUE. WATER BLUE.

BLUE FOR COTTON. COTTON BLUE. CHINA BLUE.

BLUE FOR SILK. OPAL BLUE. GUERNSEY BLUE. NIGHT BLUE.

LIGHT BLUE. BAVARIAN BLUE.

RED BLUE. SERGE BLUE. NAVY BLUE. BLACKLEY BLUE.

The Soluble blues are produced, like the Alkali blues by heating the Aniline blues, soluble in spirit, with sulphuric acid. A higher temperature ( $100^{\circ}$ ), however, is applied, and thus mixtures of di- and trisulphonic acids of diphenyl rosaniline and triphenyl pararosaniline are obtained, the sodium or ammonium salts of which form the commercial Soluble blues. As is the case with the Alkali blues, the greenest Aniline blues yield the greenest Soluble blues. In addition to this circumstance the purity and the richness of the shade depend upon the degree of sulphonation; the trisulphonates yield less pure and less intense shades than the disulphonates, while both are inferior to the Alkali blues. The disulphonates are less soluble in pure water than the trisulphonates, and it is sometimes advisable to add some soda to the colour solution, to begin the dyeing without the addition of acid, and to acidulate the bath only after the goods have been worked for some time. The disulphonates can be detected by the fact that they are precipitated from their aqueous solutions by dilute acids.

Of the various blues named above the *Bavarian blues* (produced from diphenylamine blue), *Blue for silk*, and *Opal blue* are chiefly used for silk dyeing, and give more or less greenish-blue shades; the other blues are principally dyed on wool, but they are also applied to silk and cotton. The

trisulphonates are better adapted for wool dyeing and the disulphonates for silk dyeing; no strict distinction, however, is made.

The last-named blues, *Red-blue*, &c., are the reddest products.

The shades are also distinguished by letters, from 4 R to 6 B, and the qualities by the numbers OO, O, I, II, III, IV; number OO being the purest and greenest product, the others being successively duller and redder. The prices of the Soluble blues vary widely, and the value of the different commercial products can only be determined by comparative dye trials.

The Soluble blues show the following general reactions:—Blue powders or irregular lumps; aqueous solution, blue; HCl, not much change, or blue precipitate (see above); NaOH, claret-red to red-brown: solution in  $H_2SO_4$ , brownish-yellow to brown-red; on diluting, blue solution or blue precipitate.

On reduction, the Soluble blues form leuco-compounds which are reconverted into the original dyestuffs by oxidising agents. The constitution of the coloured compounds is probably analogous to that of Acid magenta.

*Application.*—The Soluble blues are dyed both on the vegetable and animal fibres.

Cotton is dyed by various methods, but the shades produced are not fast. Since the introduction of Methylene blue and Victoria blue this fibre has been dyed to a very limited extent only with Soluble blues.

*First Method.*—Dye without previous mordanting in a very concentrated bath with the addition of 5 grms. ( $\frac{1}{2}$  lb.) alum and 20 grms. (2 lbs.) Glaubersalt per litre (10 galls), enter at  $60^\circ$  C. and allow to cool in the bath; wring off well and dry without rinsing. Loose shades only are obtained.

*Second Method.*—Mordant first in a warm soap-bath containing  $2\frac{1}{2}$  grms. (4 oz.) of soap per litre (10 galls.), working the cotton in the warm bath for 15 minutes, wring, and pass without washing into a bath of stannic chloride ( $4^\circ$  Tw.), work for half an hour, and wash thoroughly in water. Dye in a lukewarm bath, with the addition of 2 to 3 per cent. of alum. The shade is greener than that obtained by the preceding method, and fairly fast to light; it does not resist washing or soaping.

*Third Method.*—Mordant with tannin, and fix with basic alum ( $2^\circ$  Tw.), (p. 459), wring without washing and dye, heat slowly to  $60^\circ$  or  $70^\circ$ . Or the cotton is mordanted with tannin alone, and dyed with the addition of 2 to 4 per cent. of alum. No fast shades are obtained.

*Fourth Method.*—Mordant with tannin and antimony as indicated for the basic colours (p. 459), and dye in a lukewarm bath with the addition of 2 to 3 per cent. of alum, heat to  $60^\circ$  to  $70^\circ$ , wring and dry, without washing. The shade is not fast.

As the dye-bath is never exhausted it should be preserved for further use.

Wool is dyed with the addition of 2 to 4 per cent. of sulphuric acid, and 15 per cent. of Glaubersalt. By the addition of a small quantity of stannic chloride and alum, brighter shades are produced. Add the colour solution to the tepid bath, introduce the goods, heat slowly to the boil, boil for half an hour, allow to cool to  $80^\circ$ , wash and dry.

Soluble blue on wool is slightly inferior to Alkali blue in fastness to light and milling. Soluble blues are used largely for the production of navy blues on heavy woollen goods, especially so in combination with logwood.

Silk is dyed with the Soluble blues in a boiled-off liquor bath, which has been slightly acidulated with sulphuric acid. Add the colour solution to the bath, heat slowly to the boiling point, and maintain this temperature until the desired shade is obtained; wash, brighten in sulphuric acid, and dry.

Jute is dyed with the addition of  $\frac{2}{3}$  to  $1\frac{1}{2}$  per cent. of alum, and  $\frac{1}{2}$  to  $\frac{1}{3}$  per cent. of sulphuric acid; boil for 20 to 25 minutes, allow to cool to  $40^\circ$  to  $60^\circ$ , wring and dry without washing.

**HOECHST NEW BLUE (M.L.B.).**

This dyestuff is totally different from the basic New blues, and belongs to the class of "Soluble blues" just described. For its production trimethyl-triphenylpararosaniline is prepared by the action of phosgene gas ( $\text{COCl}_2$ ) on methyldiphenylamine; and the compound thus obtained is converted with sulphuric acid into a mixture of sulphonic acids. The commercial article is the lime salt of the disulphonic and trisulphonic acid.

Dark blue powder; aqueous solution, blue;  $\text{HCl}$ , blue solution and some precipitate;  $\text{NaOH}$ , decolourised; solution in  $\text{H}_2\text{SO}_4$ , brown-red; on diluting, blue solution and precipitate.

*Application.*—Hoechst new blue is chiefly used in wool dyeing. It can be dyed by the same methods as the Soluble blues. The following mode of procedure, however, is advisable, since the dyestuff is very apt to dye unevenly.

Dye for two to three hours in a boiling neutral bath with about one-third more of colouring matter than the shade requires, rinse, and develop in a fresh acid bath. The dye-bath is not exhausted and is used continuously. This method is the best for goods which are apt to dye unevenly.

Loose wool and other goods are dyed with advantage by the fourth and fifth methods given in the beginning of this chapter (p. 513); the dye-bath is fairly well exhausted. The sixth method (p. 514) also gives very good results, but the bath is not so well exhausted.

Hoechst new blue dyes pure blue shades on wool, which are moderately fast to light and fairly fast to milling.

Silk is dyed in a boiled-off liquor bath which has been slightly acidulated with sulphuric acid. Add the colour gradually to the lukewarm dye-bath and heat gradually to the boiling temperature; boil a short time, wash, brighten with sulphuric acid, wring, and dry.

**HELVETIA BLUE (Geigy).**

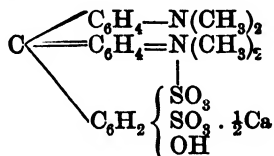
Helvetia blue is produced by condensation of 2 molecules of diphenylamine sulphonic acid with 1 molecule of formaldehyde and oxidation of the product with a third molecule of diphenylamine sulphonic acid. It has the composition of a Soluble blue.

Blue powder; aqueous solution, blue;  $\text{HCl}$ , dark blue;  $\text{NaOH}$ , decolourised; solution in  $\text{H}_2\text{SO}_4$ , brown-red; on diluting, blue solution.

*Application.*—Same as Soluble blue. Helvetia blue easily crystallises from its aqueous solution, especially in the presence of acid, and is then liable to produce an undesirable coppery gloss on the fibre. It should, therefore, be dissolved in a large quantity of water. It is chiefly used in silk dyeing, and yields very fine greenish-blue shades.

**PATENT BLUE (M.L.B.).**

Patent blue comes into the market in several brands (superfine, extra, A, B N, V, &c.), which are calcium salts of sulphonic acids of metaoxy-, meta-amido-, or metachlor-tetraalkyldiamidotriphenylcarbinol. Their constitution is exemplified by the formula:—



For their production one equivalent of metanitrobenzaldehyde is condensed with two equivalents of dimethyl- or diethyl-aniline or ethylbenzylaniline; the product is reduced so as to convert the nitro-group into the amido-group,

which, by treatment with nitrous acid, &c., may be replaced by the hydroxyl group, chlorine, &c.; by subsequent sulphonation and oxidation of the leuco-compounds the colouring matters are obtained.

Blue or coppery-red powder; aqueous solution, blue; HCl, olive-green to yellow; NaOH, makes more bluish; on heating, violet; solution in  $H_2SO_4$ , pale yellow; on diluting, deep yellow to greenish-blue.

*Application.*—The Patent blues are used for the dyeing of wool and silk, and are applied by the usual methods employed for the acid dyestuffs. They dye very evenly and well penetrate the goods; the materials may be introduced into the boiling bath. The shade is somewhat sensitive to the action of copper salts. The baths are not well exhausted and should be kept concentrated. For silk dyeing not too much sulphuric acid should be used for the acidifying of the boiled-off liquor, otherwise the shade will be less pure.

The colours can also be dyed on chromium mordants.

The Patent blues produce pure blue to greenish-blue shades which do not lose in purity and brightness, and do not appear redder but greener in artificial light. They are moderately fast to light, and fairly fast to washing; the shades are not very sensitive to dilute alkalis. Patent blue A possesses very good fastness to milling. The Patent blues are used for blue and compound shades on yarns and to a smaller extent on loose wool, but owing to their excellent levelling properties they are used chiefly on piece goods.

#### CYANINE B (M.L.B.).

This colouring matter is produced by oxidising one of the Patent blues by means of ferric salts or chromic acid; its exact constitution is not yet known. It is very similar to the Patent blues.

*Application.*—Same as other acid colours. Calcareous water should be acidulated with acetic acid before the sulphuric acid or bisulphate is added; otherwise the colours will be dull and dirty. Cyanine B dyes evenly, and produces a bright greenish-blue, similar to the Patent blues in appearance and properties; the tone, however, does not appear to vary so much in artificial light.

#### KETONE BLUE R, G, B, 4 BN (M.L.B.).

Ketone blue is very similar by its chemical constitution to Patent blue.

*Ketone blue 4 BN.*—Dark blue powder or solution; HCl, light green; NaOH, red-brown; solution in  $H_2SO_4$ , reddish-yellow; on diluting, bluish-green.

*Application and Properties.*—Same as Patent blue. Ketone blue dyes pure shades of blue and resembles in levelling properties and fastness the Patent blues.

#### CYANOL (Cassella).

Cyanol is produced by condensation of *m* oxybenzaldehyde with monoethyl *o* toluidine, sulphonation of the leuco base and oxidation of the product. It also resembles by its chemical constitution the Patent blues.

Blue powder; aqueous solution, blue; HCl, green to brown; NaOH, redder; solution in  $H_2SO_4$ , brownish-yellow; on diluting, at first green, then blue.

*Application.*—Cyanol is used for dyeing wool and silk in acid baths. It dyes very fine blues of exceptional purity and brightness, which do not change much in artificial light. It levels very well, and is chiefly used for blue, plum, olive, and other mixed shades, especially on piece goods. It is moderately fast to light, fairly fast to washing, and good to acids, alkalis, and stoving. Of the various brands Cyanol FF dyes the purest blue and Cyanol extra also very fine blues, whereas Cyanol AB is not quite as bright.

#### ERIOGLAUCINE A (Geigy).

Erioglaurine A also belongs to the Patent blue group and is produced by

condensation of benzaldehyde *o*-sulphonic acid with ethyl benzyaniline sulphonic acid and oxidation of the leuco product.

Coppery-blue powder; aqueous solution, greenish-blue; HCl, greener to yellowish-green, dark red in transparent light; NaOH, no change, on boiling, red-violet; solution in H<sub>2</sub>SO<sub>4</sub>, pale yellow; on diluting, at first darker, then green and greenish-blue.

*Application and Properties.*—Same as Patent blue. Erioglaurine dyes beautiful greenish-blue shades on wool and silk; it levels well, and is moderately fast to light, fairly fast to washing, and fast to acids and alkalies.

#### ERIOCYANINE A (Geigy).

Eriocyanine A is produced by condensation of tetramethyldiaminobenzhydrol sulphonic acid with dibenzyaniline sulphonic acid and oxidation of the leuco product.

Coppery reddish-blue powder; aqueous solution, blue; HCl, yellowish-green, brown with excess; NaOH, no change, red-violet on boiling; solution in H<sub>2</sub>SO<sub>4</sub>, light brown; on diluting, light green and then light blue.

*Application and Properties.*—Same as Erioglaurine and Patent blue. Eriocyanine A dyes a bright reddish-blue moderately fast to light, fairly fast to washing, and fast to acids and alkalies.

#### BIEBRICH ACID BLUE (Kalle).

This is a dyestuff of the triphenylmethane series, which resembles the preceding colouring matters.

Dark blue powder; aqueous solution, greenish-blue; HCl, yellowish-green, with excess, brown; NaOH, no change, on boiling, brown-red; solution in H<sub>2</sub>SO<sub>4</sub>, brown; on diluting, at first yellow, then green, and finally blue.

*Application and Properties.*—Same as Patent blue. Biebrich acid blue levels well, and dyes a bright greenish-blue, moderately fast to light, fairly fast to washing, and good to acids and alkalies. In a boiling bath it dyes both wool and silk well, but at 50° to 70° C. it dyes chiefly the silk, and thus it may serve both for dyeing uniform shades on wool and silk mixed goods and for producing two-coloured effects in the piece.

#### NEW PATENT BLUE B, 4 B, G (Bayer).

These dyestuffs are produced by condensation of tetramethyldiaminobenzhydrol with 1 : 4 or 1 : 5 naphthylamine sulphonic acid and substitution of the amino-group by a sulpho-group SO<sub>3</sub>H.

*New Patent Blue 4 B.*—Blue powder; solution, blue; HCl, yellowish-green, brown with excess; NaOH, bluish-green, on heating, red-violet; solution in H<sub>2</sub>SO<sub>4</sub>, brownish-yellow; on diluting, at first brown, then green, and finally blue.

*Application and Properties.*—Same as Patent blue. The New patent blues level well, and dye fine blue to greenish-blue shades moderately fast to light, fairly fast to washing, and fast to acids and alkalies.

#### ACID BLUE B and R (Sandoz).

These dyestuffs belong, like the preceding, to the diphenylnaphthylmethane series of colouring matters.

Blue powder; aqueous solution, blue; HCl, blue precipitate, with excess, green to red-brown solution; NaOH, no change, on boiling, pale blue (R) or violet (B); solution in H<sub>2</sub>SO<sub>4</sub>, red-brown; on diluting, bluish-green.

*Application.*—Acid blue is dyed in an acid bath on wool and silk and levels well. Acid blue R dyes a reddish-blue, in dark shades navy blue, the B brand a somewhat brighter, more greenish-blue. The shades are moderately fast to light, fairly fast to washing, and fast to acids and alkalies.

#### DISULPHINE BLUE, M, 2 M, G (Holliday).

Blue powder; aqueous solution, blue; HCl, olive-green; NaOH, almost decolourised; solution in H<sub>2</sub>SO<sub>4</sub>, yellow; on diluting, blue through olive-green.

*Application.*—These are also levelling dyestuffs, which dye bright shades of blue of moderately good fastness to light, washing, milling, acids, and alkalies. They are used in acid baths on wool and silk, and may also be used in neutral baths for shading the wool in dyeing unions with direct cotton colours by the one-bath method.

**WOOL BLUE N, R, SR EXTRA (Bayer). BRILLIANT WOOL BLUE B EXTRA (Bayer).**

These dyestuffs are derivatives of diphenyl-naphthylmethane.

*Wool Blue N Extra.*—Coppery-blue powder; aqueous solution, blue; HCl, dark green; NaOH, dull red-violet; solution in  $H_2SO_4$ , red; on diluting, at first brown, then green, and eventually blue.

*Application.*—The Wool blues dye wool in an acid or neutral bath, and are distinguished for their good fastness to washing, milling, acids, alkalies, and stoving, while they are moderately fast to light. They dye pure shades of blue which are useful for yarns and piece goods. As they dye very well in a neutral bath, they are also very useful for dyeing wool in unions in combination with direct cotton colours by the single-bath method. Silk is dyed in acid liquors, the shades produced possessing good fastness to water.

**WOOL BLUE 5 B, 2 B, R, G EXTRA (Berlin). NEUTRAL BLUE R, 3 R (M.L.B.).**

These dyestuffs behave similarly to the above Wool blues and are used for the same purposes.

**BRILLIANT MILLING BLUE B (Cassella).**

This is a triphenylmethane dyestuff which shows the following reactions:—Violet-blue powder; aqueous solution, violet-blue; HCl, olive; NaOH, little change, on heating, slowly decolourised; solution in  $H_2SO_4$ , yellow; on diluting, green.

*Application.*—Brilliant milling blue B shows similar properties to the preceding Wool blues and dyes very pure shades of violet-blue in acid or neutral baths on wool, silk, and unions, which are very fast to milling and washing, acids, alkalies, and stoving, and moderately fast to light.

**GALLANILIC INDIGO PS (Durand).**

This colour is related to Gallocyanine, Gallanilide violet, and Gallanilide blue. For its production Gallanilide is heated with nitrosodimethylaniline; the product is subsequently phenylated by treatment with aniline, and finally converted into a sulphonic acid.

Dark blue paste; aqueous solution, indigo blue; HCl, dark brown precipitate; NaOH, soluble blue precipitate; solution in  $H_2SO_4$ , brown; on diluting, brown precipitate.

*Application.*—Gallanilic indigo PS is dyed on wool with the addition of sulphuric acid and Glaubersalt, and yields very fine shades resembling those of Indigo carmine, but faster to light.

**THIOGARMINE R (Cassella).**

Thiocarmine R is chemically related to Methylene blue, being a sulphonated thionine. It is prepared analogously to New methylene blue N by using ethyl- and aminoethylbenzylaniline sulphonic acid in place of ethyl- and aminoethyl-toluidine.

Dark blue paste or red-blue powder; aqueous solution, bluish-green; HCl, no change; NaOH, no change, on heating, violet; solution in  $H_2SO_4$ , bright green; on diluting, deep blue.

*Application.*—Same as the other acid colours. Thiocarmine dyes greenish-blue shades on wool. It dyes evenly, and is suitable for the production of compound shades, modes especially. The shade is inferior to Patent blue or Cyanol in resistance to light, and moderately fast to milling, fast to acids and alkalies.

**INDULINE** (soluble in water). **FAST BLUE. INDIGO SUBSTITUTE. NIGROSINE.**

The *Indulines and Nigrosines, soluble in spirit* (p. 490), are converted by the action of sulphuric acid into sulphonic acids, which are soluble in water, and can then be dyed by the same methods as the acid colours.

The commercial brands, which give various shades of dark indigo blue, are known as Fast blue R to 3 R or Induline N N for the reddish shades, and Fast blue B or greenish, and Induline 3 B and 6 B for the blue shades. Nigrosine, which also belongs to these dyestuffs, dyes greyish-blue shades.

Brown to black powder, with a bronze lustre; aqueous solution, violet-blue; HCl, more bluish, or a blue precipitate is formed; NaOH, soluble brown-violet precipitate; solution in  $H_2SO_4$ , blue; on diluting, violet-blue, or blue precipitate.

Induline forms on reduction a leuco-compound, which is reoxidised by the action of the air.

The degree of sulphonation of the commercial products varies; some resemble Alkali blue and can be dyed in a similar manner; most brands are more similar in this respect to the Soluble blues.

*Application.*—Induline is used to a small extent in cotton dyeing, more for wool, but principally for silk dyeing.

Cotton is mordanted with tannin and antimony and dyed at the boil with the addition of a little sodium bisulphate. A dark indigo blue shade is obtained which does not resist washing well, but is very fast to light.

The colour can also be fixed to some extent on unmordanted cotton.

*Wool.*—The Indulines show a singular behaviour towards the wool fibre\* which is apparently founded on their chemical constitution. They produce no patches like other "uneven" colouring matters; it is the single wool fibre which is dyed unevenly by the Indulines, as can be seen under the microscope; the roots of the wool fibres take up the colour pretty easily, whilst the more horny portions take it up very slowly or not at all. The speckled effect thus produced, which is called "*piqué*" by the French dyers, has prevented the general employment of these dyestuffs. Coarse wools dye better with the Indulines than the fine qualities. If the wool be boiled in dilute solutions of soda, borax, or sodium stannate, it will afterwards dye more easily with Induline. This method, however, has not found favour with dyers, who naturally fear the injurious effect of hot alkaline liquids on wool. Another method, used especially in wool-printing, consists in chlorinating the wool by steeping it alternately in a dilute solution of bleaching powder and dilute hydrochloric acid. Wool treated in this manner undergoes a great change and is rendered somewhat similar to silk; it loses, however, greatly in milling capacity (see p. 56).

To obtain even colours on wool slow and very hot dyeing is of great advantage. If the Induline is only slightly soluble in acidulated water the method indicated for Alkali blue may be employed. The readily soluble Indulines are dyed in a rather concentrated neutral bath, and after the goods have been boiled for some time, 5 per cent. of sodium bisulphate is gradually added. It is, however, advisable to use in this case also a separate bath with sodium bisulphate, since the dye-bath is not well exhausted.

Dark indigo shades are obtained by the following method:—Dye in a bath containing 2 to 5 per cent. of Induline and 5 per cent. of ammonium oxalate (or 3 per cent. of oxalic acid), heat to the boiling point, and boil for two to three hours, wash, and enter into a hot bath containing 5 per cent. of sodium bisulphate. The colour is almost entirely developed in the first bath; in the second bath the blue can be shaded with other acid dyestuffs.

\* O. N. Witt, *Journ. Soc. Dyers and Col.*, 1890, p. 42.



Induline yields dark indigo blue shades which are moderately fast to light and milling; they are not sensitive to acids and alkalies.

Silk does not offer the same difficulties to dyeing with Induline as wool. It is dyed in a boiled-off liquor bath which has been made distinctly acid with sulphuric acid. Add the colour solution, raise the temperature to the boiling point, work for half an hour, wash, and brighten with sulphuric acid, wring, and dry.

Induline has replaced Indigo carmine to a very great extent in the production of mixed shades on silk, since it is very fast to light.

#### **NAPHTHAZINE BLUE** (Dahl, M.L.B.).

Naphthazine blue is produced by the action of nitrosodimethylaniline upon the disulphonic acid of betadinaphthyl *m* phenylene diamine, and belongs to the group of azine colouring matters.

Violet-brown powder; aqueous solution, blue-violet; HCl, blue precipitate; NaOH, no change; solution in H<sub>2</sub>SO<sub>4</sub>, dark green; on diluting, blue precipitate.

*Application*.—Naphthazine blue is dyed on wool in an acid bath, according to Method I., p. 513. Some care is necessary to obtain even shades. It dyes dark navy blues of fairly good fastness to light and milling, and good fastness to acids and alkalies. The fastness to milling may be improved by treating the dyed wool in a fresh bath with 1 to 3 per cent. bichromate. Silk is dyed in a boiled-off liquor acidulated with sulphuric acid, or in a bath containing acetic acid which is exhausted by adding sulphuric acid. Naphthazine blue is, owing to its good fastness, useful for dark shades on silk. Wool and silk mixed goods are dyed fairly solid shades with Naphthazine blue.

#### **URANIA BLUE** (Dahl).

Urania blue is produced by conjoint oxidation of *p* aminodimethylaniline thiosulphonic acid and betadinaphthyl *m* phenylene diamine disulphonic acid. Its constitution is not known.

Indigo blue powder; aqueous solution, blue; HCl, soluble dark blue precipitate; NaOH, no change; solution in H<sub>2</sub>SO<sub>4</sub>, dark green; on diluting, blue.

*Application and Properties*.—Same as Naphthazine blue. Urania blue dyes purer and greener shades of blue, and is chiefly recommended for dyeing silk, on which fibre it yields colours which stand the water-test.

#### **INDOCYANINE B** (Berlin).

Indocyanine B is the sulphonate of a phenylated compound of the rosinduline-group.

Dark blue powder; aqueous solution, violet-blue; HCl, dark precipitate and red-violet solution; NaOH, violet-red precipitate and solution; solution in H<sub>2</sub>SO<sub>4</sub>, green; on diluting, red-violet.

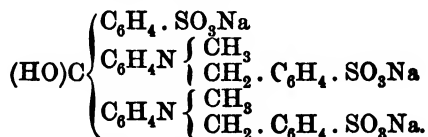
*Application*.—Indocyanine is dyed on wool in a neutral or, better, in a feebly acid bath, best with the addition of 15 per cent. ammonium acetate (30 per cent. solution) or 5 per cent. ammonium sulphate. Bring the bath to the boil, shut off the steam, enter the goods, and dye with continuous boiling. The dyestuff does not dye well below the boiling temperature, and does not exhaust perfectly. 2 to 3 per cent. of acetic acid may be added towards the end of the dyeing process to exhaust the bath better. Impure materials are best boiled, before dyeing, with  $\frac{1}{2}$  per cent. sulphuric acid and 1 per cent. bichromate, then well rinsed, and dyed with the addition of 10 per cent. Glaubersalt. For shading, any dyestuff working well in a neutral or feebly acid bath may be used. The dyestuff may also be used together with mordant colours, acid chrome colours, and metachrome colours.

Indocyanine B dyes full indigo blue shades on wool, which are very fast to light and washing, good to acids and alkalies, and resist a light milling well.

Silk is dyed with or without boiled-off liquor in a bath acidulated with

acetic acid. Unions may be dyed with Indocyanin, and direct cotton colours by the one-bath method.

**LIGHT GREEN S F (BLUISH) (B.A.S.F.). ACID GREEN.**



**LIGHT GREEN S F (YELLOWISH) (B.A.S.F.). ACID GREEN. ACID GREEN D or EXTRA CONC.**

Ethyl-compound, analogous to Light green S F (bluish).

Light green S F, bluish and yellowish, are the disulphonic acids of certain compounds of the benzaldehyde green group. For their production one equivalent of benzaldehyde is heated with two equivalents of benzylmethyl-aniline or benzyloethylaniline respectively, and the products are sulphonated with fuming sulphuric acid. Thus the leuco-compounds are obtained which are converted into the colouring matters by oxidation.

Light green S F (bluish) forms a brown-black powder, Light green S F (yellowish) a light green powder. Both show the following reactions:—Aqueous solution, green; HCl, brownish-yellow; NaOH, decolourises and produces a dirty violet turbidity; solution in  $\text{H}_2\text{SO}_4$ , brownish-yellow; on diluting, green.

*Application.*—According to general methods (p. 513, *et seq.*), the Light greens dye pure green shades similar to, but yellower than, Malachite green, which are moderately fast to light and milling; they are very sensitive to the action of dilute alkalis, but not to dilute acids. The Light greens, owing to their rich, brilliant shades, are used very extensively for bright greens—*eg.*, for billiard cloth—and in combination with the Acid violets for blues on ladies' dress goods, &c.; but, on account of their moderate fastness to light and their sensitiveness to alkalis and alkaline road dirt, their use should be limited to such purposes only where fastness to light and alkalis is of no consideration, faster and nearly equally bright greens being now in the market (see below).

**ACID GREEN EXTRA CONC. B (Cassella)** is a sulphonic acid of diphenyl dibenzyl-diaminotriphenylcarbinol of the same properties as the preceding Light greens or Acid greens, and yields pure shades of bluish-green.

**GUINEA GREEN B (Berlin).**

This colouring matter is produced by heating benzaldehyde with ethyl-benzylaniline sulphonic acid, and oxidising the leuco-compound thus obtained. It resembles by its constitution the preceding greens.

Dark green powder; aqueous solution, green; HCl, green; NaOH, black-green precipitate; solution in  $\text{H}_2\text{SO}_4$ , yellow; on diluting, at first yellowish-red, then yellowish-green, finally green.

*Application.*—Same as Light green.

The shade is similar to that of the Light greens, and behaves similarly towards the various agents.

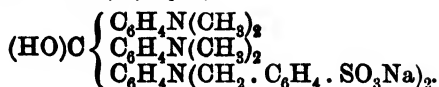
**GUINEA GREEN B V (Berlin).**

This product is the nitro-compound of the preceding substance, obtained analogously by using metanitrobenzaldehyde instead of benzaldehyde.

Blue-green powder; aqueous solution, green; HCl, blue-green precipitate; NaOH, almost decolourised; solution in  $\text{H}_2\text{SO}_4$ , brown; on diluting, yellowish-green.

*Application.*—Same as Light green.

Guinea green B V is very similar to Guinea green B, the shade is more yellowish.

**FAST GREEN (BLUISH)** (Bayer).

By heating metanitrobenzaldehyde with dimethylaniline, nitro-malachite-green is prepared; this compound is reduced, the amino-group of amino-leuco-malachite-green thus formed is benzylated, and the product sulphonated and oxidised to form the colouring matter.

Dark bluish-green crystalline powder; aqueous solution, blue-green; HCl, yellow; on diluting, blue-green; NaOH (on heating only), decolourised; solution in  $\text{H}_2\text{SO}_4$ , yellowish-red; on diluting, olive to blue-green.

*Application.*—Wool is dyed according to Method I. (p. 513). Fast green (bluish) dyes on wool a fairly bright bluish-green, which is fairly fast to light and milling, and not sensitive to dilute acids and alkalis. It levels well, and is chiefly used for compound shades on yarns and piece goods. Silk is dyed in an acid bath, fairly fast to light, water, acids, and alkalis.

**FAST GREEN EXTRA BLUISH** (Bayer) and **FAST LIGHT GREEN** (Bayer) are similar to Fast green (bluish), and dye bluer shades of green.

**WOOL GREEN S** or **BS** (B.A.S.F., Ch. Ind. Basle, Sandoz, Bayer).

Wool green S is produced by condensation of tetramethyldiaminobenzophenone chloride and betanaphthol and sulphonation of the product. It is a derivative of diphenylnaphthylmethane.

Red-brown powder; aqueous solution, greenish-blue; HCl, greener, in excess yellow; NaOH, little change, on boiling passes through violet to pink; solution in  $\text{H}_2\text{SO}_4$ , dull violet; on diluting, yellow to green.

*Application.*—Wool and silk are dyed in acid baths with the addition of sulphuric acid. The dyestuff levels well, and yields bluish-green shades fairly fast to light and washing, and good to acids and alkalis. It is an exceedingly useful dyestuff for the production of compound shades on yarn, and especially on piece goods.

**BLUE GREEN S** (B.A.S.F.), **NEPTUNE GREEN S, SB, SBN** (B.A.S.F.), **CYANOL GREEN B** and **6 G** (Cassella), and **KITON GREEN S** (Ch. Ind. Basle) are similar to Wool green S, and are used for the same purposes.

**NAPHTHALENE GREEN V** (M.L.B.).

This dyestuff is also a derivative of diphenylnaphthylmethane.

Brown powder; aqueous solution, green; HCl, brown; NaOH, little change; on boiling, decolourised; solution in  $\text{H}_2\text{SO}_4$ , yellowish-brown; on diluting, yellow.

*Application.*—Naphthalene green dyes a bright green, similar to and almost as bright as Acid green (Light green). It is dyed in sulphuric acid baths on wool and silk, and levels well. In fastness it is superior to the preceding greens; it is very satisfactory in fastness to light and washing, and good to acids and alkalis, faster indeed to alkalis than Wool green, &c.

**CYANOL FAST GREEN G** (Cassella).

Cyanol fast green G is also a derivative of diphenylnaphthylmethane.

Dull green powder; aqueous solution, bluish-green; HCl, yellowish-olive; NaOH, slightly bluer; on heating, violet-blue; solution in  $\text{H}_2\text{SO}_4$ , yellow; on diluting, lighter.

*Application and Properties.*—Same as Naphthalene green.

**ALKALI FAST GREEN B, G, 3 B, 3 G** (Bayer).

These dyestuffs are also derivatives of diphenylnaphthylmethane.

*Alkali fast green B.*—Dark powder; aqueous solution, green; HCl, brown; NaOH, little change; on boiling, bluish-violet; solution in  $\text{H}_2\text{SO}_4$ , pale green; on diluting, brown-yellow.

*Application and Properties.*—Same as Naphthalene green.

**BRILLIANT MILLING GREEN B** (Cassella).

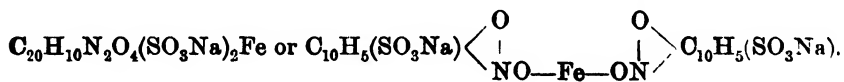
This is a triphenylmethane dyestuff, which shows the following reactions:—

Dark blue powder; aqueous solution, greenish-blue; HCl, brown solution and dark precipitate, soluble with a blue colour; NaOH, greener; on heating, light violet; solution in H<sub>2</sub>SO<sub>4</sub>, brownish; on diluting, at first yellow, then green, and finally blue.

*Application.*—Brilliant milling green B is dyed on wool in acid baths, with the addition of sulphuric or acetic acid, like the other acid colours (p. 512); it may also be dyed on chromed wool, like the mordant dyestuffs; or may be chromed, after dyeing, in combination with the acid chrome colours. It also works fairly well in a neutral bath, and is therefore also applicable for dyeing wool in various goods dyed with direct cotton colours by the one-bath method. Brilliant milling green dyes a bright bluish-green, moderately fast to light, and very fast to milling and acids. The colour withstands heavy milling very well; the goods should, however, be soured off after alkaline milling. The fastness to alkalies is satisfactory, although not quite so good as that of the preceding greens (Naphthalene green, Cyanol fast green, and Alkali fast green), whereas the fastness to milling is superior. Dyed on chromed wool or after-treated with bichromate, Brilliant milling green is rendered slightly duller, but its fastness to milling is increased. The dyestuff serves well for dyeing greens and mixed shades on wool fast to milling, especially in combination with acid colours, acid chrome colours, and mordant colours, and, as indicated above, it is also very useful for dyeing unions. Silk is dyed in boiled-off liquor acidulated with sulphuric acid. The colour is very good to washing and water, and is still improved in fastness by a treatment with tannin and antimony after dyeing (see p. 191).

**NEPTUNE GREEN S G** (B.A.S.F.). **BENZYL GREEN B** (Ch. Ind. Basle). **FAST WOOL GREEN B** (Kalle). **BRILLIANT ACID GREEN 6 B** (Bayer) are similar to, or identical with, the preceding dyestuff.

**NAPHTHOL GREEN B** (Cassella). **GREEN P L** (B.A.S.F.).



Naphthol green may be considered to be an iron-compound of a sodium sulphionate of nitroso-betanaphthol. It is produced by the action of nitrous acid on betanaphtholsulphonic acid (Schäffer) in the presence of an iron salt. The iron is in intimate combination with the organic compound and cannot be readily detected by the usual means; if the substance is heated on platinum foil, ferrous sulphide is obtained.

Naphthol green is a dark green powder, freely soluble in water, with a dark yellowish-green colour. The aqueous solution is not changed in the cold by hydrochloric acid, but becomes yellow when heated with this reagent, and yields blue precipitates with yellow or red prussiate. Caustic soda does not change the colour of the solution. The solution in sulphuric acid is brownish-yellow; it becomes yellow on diluting, and it then shows the iron reaction with the prussiates.

*Application.*—Naphthol green is dyed on unmordanted wool and silk.

Wool is dyed in an acidulated bath by the first method (p. 512); for a full shade more than 5 per cent. of Naphthol green and 4 per cent. of sulphuric acid are required. The goods are entered cold and the temperature is slowly raised to the boil. Naphthol green dyes an olive-green; it is distinguished by fastness to light, washing, milling, acid, and alkalies. It is

very useful for dark greens, olives, &c., on piece goods, carpet yarns and other goods which are required to be dyed very fast to light and washing. Silk is dyed with the addition of acetic acid, and the bath is exhausted with sulphuric acid.

**CYPRUS GREEN B** (Berlin).

Dark brown powder; aqueous solution, red-violet; HCl, gelatinous brown precipitate; NaOH, blue-violet solution and soluble precipitate; solution in  $H_2SO_4$ , violet-red; on diluting, red solution and precipitate.

*Application.*—This azo-dyestuff is applied exactly like Cyprus blue R (p. 543), and dyes on wool dark green shades of very good fastness to light, washing, acids, and alkalis, which are also very satisfactory to milling. It may also be dyed in combination with acid chrome colours and metachrome colours.

**NAPHTHYLAMINE BROWN** or **FAST BROWN N** (B.A.S.F.). **AZO-BROWN O** or **CHROME BROWN R O** (M.L.B.).

Naphthionic acid—alpha-naphthol.

Dark brown powder; aqueous solution, yellowish-brown; HCl, dark brown precipitate; NaOH, red-brown; solution in  $H_2SO_4$ , blue; on diluting, brown precipitate.

*Application.*—Same as the other acid dyestuffs on wool and silk (p. 513, *et seq.*).

Naphthylamine brown dyes an orange-brown, which lacks brilliancy and brightness, and is not fast to milling, but fairly fast to light. It is converted into a deeper and more bluish-brown of great fastness to milling when treated according to the process of the Farbwerke Hoechst (M.L.B.) with 3 per cent. bichromate and 1 per cent. sulphuric acid for one to one and a-half hours in a boiling bath.

**FAST BROWN** (Bayer).

Naphthionic acid  
Naphthionic acid } resorcin.

*Application.*—Same as the other acid dyestuffs on wool and silk (p. 513, *et seq.*).

Fast brown dyes a good reddish-brown of moderate fastness to light and washing, and good fastness to acids and alkalis. It is recommended for dyeing on chromed wool, and applied in this way yields a brown faster to milling, but the fastness to light is not improved by this treatment.

**FAST BROWN O N T** yellow shade (M.L.B.).

Xylidine sulphonic acid  
Xylidine sulphonic acid } alpha-naphthol.

Dark brown powder; aqueous solution, brown; HCl, violet precipitate; NaOH, reddish-yellow; solution in  $H_2SO_4$ , violet; on diluting, red.

*Application.*—Fast brown is dyed on wool and silk in the same way as the other acid colours. As it is liable to dye uneven, the dyeing of wool should be started at about 40° in a neutral bath, and sodium bisulphate be added very gradually in small portions. Fast brown produces a moderately fast brown-red shade, which is not very brilliant.

**FAST BROWN G** (Weiler ter Meer). **ACID BROWN** (Dahl).

Sulphanilic acid  
Sulphanilic acid } alpha-naphthol.

Brown powder; aqueous solution, red-brown; HCl, soluble violet precipitate; NaOH, cherry-red; solution in  $H_2SO_4$ , violet; on diluting, yellowish-brown.

*Application.*—Fast brown G resembles the preceding brown, and is applied in the same way. It yields yellowish-brown shades.

**FAST BROWN 3 B** (Berlin).

Beta-naphthylamine sulphonic acid (Br)—alpha-naphthol.

Brown powder; aqueous solution, brown-red; HCl, red-violet; NaOH, crimson; solution in  $H_2SO_4$ , blue; on diluting, red-violet precipitate.

*Application.*—Fast brown 3 B is similar to the two preceding Fast browns, and is applied in the same way. It dyes reddish-brown shades.

**ORCELLIN** (Leonhardt).

Dark brown powder; aqueous solution, claret-red; HCl, little change, NaOH, more bluish; solution in  $H_2SO_4$ , dark violet; on diluting, red.

*Application.*—Wool is dyed with this dyestuff in an acid bath a dark reddish-brown, which resists hot soaping and light fairly well, and is moderately fast to milling. It can also be dyed on chromium mordants.

Silk is dyed in a boiled-off liquor bath acidulated with sulphuric acid. Enter at about  $30^\circ$ , heat slowly to the boiling point, and boil for some time. Violet-brown shades, fairly fast to light and washing, are obtained.

**RESORCIN BROWN** (Berlin, Holliday).

Xylidine—chrysoïn.

This dyestuff is obtained by the action of diazotised xylidine on the orange-yellow dyestuff Chrysoïn or Tropaeolin R (*sulphanilic acid azo-resorcin*) (p. 520).

Brown powder; aqueous solution, yellowish-brown; HCl, soluble brown precipitate; NaOH, more reddish; solution in  $H_2SO_4$ , reddish-brown; aqueous solution, brown precipitate.

*Application.*—Resorcin brown is dyed by the ordinary methods used for the acid colours (p. 513). It dyes a fine yellowish-brown shade, which is fairly fast to light and milling on wool.

**AZO-ACID BROWN R** (Bayer).

Brown powder; aqueous solution, brown; HCl, dark brown flocculent precipitate; NaOH, soluble red precipitate; solution in  $H_2SO_4$ , blue-violet; on diluting, dark brown precipitate.

*Application.*—This dyestuff seems to be closely related to Azo-bordeaux, Azo-cochineal, Azo-acid violet 4 R, and, like these, it levels well on wool. It may, therefore, be used for dyeing mode shades in an acid bath; it yields a yellowish-brown, fairly fast to light, washing, acids, and alkalis.

**SULPHONE BROWN R** (Bayer).

Dark powder; aqueous solution, brown; HCl, brown precipitate; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , violet-black; on diluting, orange-yellow precipitate.

*Application.*—Same as Sulphone cyanin (p. 541). The dyestuff is exclusively used on wool or unions, and dyes a fine dark brown.

**SULPHONE DARK BROWN**, a similar dyestuff, yields a very dark bluish-brown.

**NAPHTHOL BLACK B** (Cassella). **BRILLIANT BLACK** (B. A. S. F.).

Aminoazonaphthalene disulphonic acid—

beta-naphthol disulphonic acid (R salt).

For the production of Naphthol black B aminoazonaphthalene disulphonic acid is prepared by the action of diazotised beta-naphthylamine gamma-disulphonic acid on alpha-naphthylamine; this compound is again diazotised, and combined with beta-naphthol disulphonic acid (R salt).

Similar products are:—

**Naphthol black 2 B, 3 B, 6 B, and 4 R** (Cassella).—They are produced in

the same way, the beta-naphthylamine disulphonic acid being substituted by various isomeric acids.

The commercial products show the following reactions:—Black powder; aqueous solution, violet; HCl, violet solution or violet precipitate; NaOH, little change or soluble blue precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, pure green to olive-green; on diluting, it turns at first bluer, and subsequently yields a violet precipitate.

*Application.*—The Naphthol blacks are used almost exclusively in wool dyeing. Being tetrazo-compounds, they will, by virtue of their chemical constitution, also dye unmordanted cotton; but they possess no importance for this fibre.

Cotton may be dyed with Naphthol black both in an acid bath (with the addition of alum), and in an alkaline bath (with the addition of soap and phosphate of soda).

Wool is dyed by the same methods as with the other acid colours (p. 513). Enter at 60° to 70° into the bath prepared with 4 per cent. sulphuric acid and 20 per cent. Glaubersalt, heat within twenty minutes to the boil, and boil one hour. Then exhaust the bath by the further addition of 1 or 2 per cent. sulphuric acid, and continuing to boil twenty minutes longer. Navy blues are dyed by combining Naphthol black with Acid violet. The bath is best prepared with 5 per cent. acetic acid and 20 per cent. Glaubersalt; enter at 40°, heat slowly to the boil, and, after three-quarters of an hour boiling, exhaust by adding 2 per cent. sulphuric acid.

Naphthol black B dyes wool from dark blue to deep black; Naphthol black 6 B gives an excellent black, for a full black shade 8 to 10 per cent. of colouring matter are required. All acid colours can be used for shading; Naphthol green, Tartrazin, and Azo-flavin (Indian yellow) are especially well adapted for this purpose. The shades produced with Naphthol black on wool are equal to logwood black in beauty and in fastness to light; they are not sensitive to acids or alkalies, and resist wear and tear, but they are not fast to milling. Cotton threads (shots or selvages) next to wool are not stained when dyeing in acid baths, although Naphthol black dyes cotton in the absence of wool (see above). More recently the other acid dyeing blacks, like Naphthylamine black, Wool black, Biebrich patent black, &c., have largely superseded Naphthol black, as they dye fuller shades of black of satisfactory fastness. Naphthol black also finds extensive application in the printing of woollen tissues, and is used for re-dyeing dress goods.

Silk is not dyed with Naphthol black.

#### AZO-BLACK (M.L.B.). BLUE-BLACK B (B.A.S.F.).

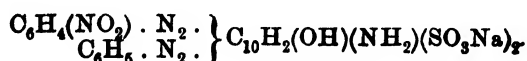
These two products are very similar in their chemical constitution and resemble Naphthol black. For their production beta-naphthylamine is sulphonated, and the mixture of acids thus obtained is diazotised and combined with alpha-naphthylamine; the product of this reaction is rediazotised and combined again with beta-naphthol disulphonic acid (R salt).

Blue-black powder; aqueous solution, blue-violet; HCl, blue precipitate; NaOH, soluble blue precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, bluish-green; on diluting, blue precipitate.

*Application and Properties.*—Same as Naphthol black.

#### NAPHTHOL BLUE-BLACK (Cassella). NAPHTHOL BLACK 12 B.

Naphthol blue-black is produced by the action of 1 molecule nitrodiazo benzene chloride and 1 molecule diazobenzene chloride on 1 : 8 aminonaphthol disulphonic acid H.



Dark brown powder ; aqueous solution, dark blue ; HCl, blue precipitate ; NaOH, no change ; solution in  $H_2SO_4$ , green ; on diluting, blue precipitate.

*Application.*—Naphthol blue-black is dyed on wool and silk like the other acid colours (p. 513, *et seq.*).

Wool is dyed as with Naphthol black. Naphthol blue-black dyes very full blue-black shades which do not change in artificial light. It possesses very good fastness to light, acids, alkalies, steaming, and stoving, and is moderately fast to washing and milling. It levels fairly well, and is very well suited for shading the various kinds of acid blacks (Naphthylamine black, &c.) Naphthol blue-black dyes wool fairly well in a neutral bath, and may consequently be used for shading the wool in union dyeing by the single-bath method.

Silk is dyed in boiled-off liquor acidulated with sulphuric acid.

**NAPHTHYLAMINE BLACK D (Cassella).**

Aminoazonaphthalene disulphonic acid—alpha-naphthylamine.

The aminoazonaphthalene disulphonic acid, required for the manufacture of this product, is prepared by the action of alpha-naphthylamine disulphonic acid on alpha-naphthylamine.

Black powder ; aqueous solution, dark violet ; HCl, dark violet precipitate ; NaOH, soluble dark violet precipitate ; solution in  $H_2SO_4$ , black-blue ; on diluting, at first green solution, and afterwards a dark violet precipitate.

*Application.*—Wool is dyed in an acid bath prepared with 5 per cent. acetic acid and 10 per cent. Glaubersalt. Enter at  $70^\circ$ , heat within twenty minutes to the boil, and after three-quarters of an hour's boiling exhaust by adding 2 to  $2\frac{1}{2}$  per cent. sulphuric acid diluted with water, continuing to boil twenty minutes longer until the bath is exhausted. The shade becomes less bloomy by beginning to dye with sulphuric acid, and in this case no more acid should be used than necessary to fix the colour—*i.e.*, 3 per cent. sulphuric acid added in two parts. Naphthylamine black D levels fairly well, and dyes violet-black shades which are fairly fast to light and milling, not sensitive to acids or alkalies, and resist a light steaming. It is much faster to washing and milling than Naphthol black, but not so fast to light. For a full black 5 to 6 per cent. of colour are necessary ; by adding Acid green, or, better, Naphthol blue-black, purer black shades are produced. Naphthylamine black D dyes wool well in a neutral bath, and is very useful for shading the wool in union dyeing by the single-bath method.

Silk is dyed in boiled-off liquor acidulated with sulphuric acid. On this fibre the colour is fairly fast to washing and water.

**NAPHTHYLAMINE BLACK 4 B, 6 B (Cassella)** are similar to the "D" brand, but yield finer shades of black, which are also slightly faster to light and steaming. They are used in very large quantities for black dyeing of wool and silk, both for piece goods and yarns, especially knitting yarns, and also for unions.

**NAPHTHYLAMINE BLACK S, E S N, &c. (Cassella)**, more resemble in properties Naphthol blue-black, and are dyed like this dyestuff in strongly acid baths. They yield fine shades of black, which are very fast to light and steaming, acids and alkalies, and moderately fast to washing, and are chiefly employed for black dyeing woollen and worsted tissues, and also yarns.

**NAPHTHYLAMINE BLACK R, R N B (Cassella)** resemble Naphthyl blue-black (see below) in application and properties, but dye jet black shades.

**NAPHTHYL BLUE-BLACK N (Cassella).**

Greyish-black powder ; solution, dark violet ; HCl, blue solution and soluble black precipitate ; NaOH, makes the solution more bluish, and produces a soluble dark precipitate ; solution in  $H_2SO_4$ , dark blue ; on diluting, at first blue, then blue-violet.



**Application.**—Naphthyl blue-black N may be dyed like Naphthylamine black D. The following process has proved exceedingly useful for the production of a fine blue-black on wool, very fast to light, heavy steaming, washing, acids, and alkalies, and also rather good to milling:—Prepare the bath with the dyestuff, 5 per cent. acetic acid, 10 per cent. Glaubersalt, and, in the case of hard water, 1 to  $1\frac{1}{2}$  per cent. oxalic acid. Enter at 60° to 70°, heat within twenty minutes to the boil, and boil one hour. Then add 3 per cent. sulphate of copper and 4 per cent. acetic acid, and work half an hour without steaming. Mineral acids would impede the effect of the treatment with copper regarding the fastness to steaming, light, washing, and milling, and must not be used in this process. Naphthyl blue-black and the similar brands, Naphthylamine black R, R N B, owing to their behaviour towards copper sulphate, may be well combined with logwood for dyeing cheap blacks superior to pure logwood blacks in fastness to light and acids. Prepare the bath with 2 to 3 per cent. oxalic acid, 10 to 20 per cent. Glaubersalt, logwood extract, and Naphthyl blue-black, boil up, shut off the steam, enter the goods, work twenty to thirty minutes without steam, and one hour at the boil. If after this time the bath has not become pale yellowish-brown, the artificial black is not yet taken up, and must be exhausted by the addition of 1 to  $1\frac{1}{2}$  per cent. more of oxalic acid, and boiling fifteen to twenty minutes longer. Then add 4 per cent. ferrous sulphate and 4 per cent. cupric sulphate, and continue boiling for three-quarters of an hour. Wash well and dry. In a similar way Naphthyl blue-black may be dyed together with sumach extract in order to produce a full black with firm handle and good weighting, as obtained by logwood-iron black.

**ANTHRACITE BLACK B** (Cassella). **PHENYLENE BLACK** (Poirrier).

Aminoazonaphthalene disulphonic acid—diphenylmetaphenylenediamine.

Brownish-black powder; aqueous solution, violet black; HCl, blue; NaOH dark violet-red precipitate; solution in  $H_2SO_4$ , blackish-blue; on diluting, brownish-olive precipitate, soluble in water with a dark blue colour.

**Application.**—Anthracite black is especially valuable for wool dyeing, and is also recommended for silk dyeing.

Wool is dyed with the addition of 10 per cent. of Glaubersalt, and 5 per cent. of acetic acid. Enter at 60°, heat within thirty minutes to the boil, and boil for three-quarters of an hour. Exhaust the bath slowly by the gradual addition of 3 to 5 per cent. sodium bisulphate. Anthracite black dyes unmordanted wool from light grey to deep blue-black, and shaded with yellow like Anthracene yellow C jet black. The colour possesses excellent fastness to light, milling, alkalies, acids, and stoving, and resists light steaming well. It may be considered as the best acid black in fastness to milling and washing. It may be dyed on chromed wool, or be after-chromed with chromium fluoride; but its good fastness to milling is hardly improved by such treatment. In combination with violets fast to milling, such as Formyl violet, the dyestuff is used for dyeing fast blues on yarns, tops, loose wool, and shoddy.

Silk is dyed in boiled-off liquor acidulated with sulphuric acid. Dark blue to black shades are obtained, which are very fast to light, water, washing, and milling, especially when after-treated with chromium fluoride.

**VICTORIA BLACK B** (Bayer).

This colouring matter is produced by combining diazotised sulphanilic acid with alpha-naphthylamine, re-diazotising and combining with (1 : 8) dioxy-naphthalene sulphonic acid.

Black powder; aqueous solution, dark violet; HCl, more reddish; NaOH, more bluish; solution in  $H_2SO_4$ , dark green-blue; on diluting, reddish-blue.

Similar dyestuffs are *Victoria black-blue* and *New Victoria black-blue* (Bayer)

*Application and Properties.*—Same as Naphthol black.

**JET BLACK R** (Bayer).

This dyestuff is produced by combining diazotised paramidobenzene disulphonic acid with alpha-naphthylamine, re-diazotising and combining with phenylalphanaphthylamine.

Black powder; aqueous solution, violet-blue; HCl, blue-black precipitate; NaOH, soluble blue-violet precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, dark reddish-blue; on diluting, dark blue-green precipitate.

*Application.*—Jet black R is dyed on wool in a feebly acid bath best with the addition of ammonium acetate and acetic acid, and on silk in a hot bath with boiled-off liquor acidulated with acetic acid. Copper vessels affect the dyestuff. Five per cent. Jet black R produces a full blue-black on wool, which is fairly fast to light and milling, and good to acids and alkalis. Darker shades are obtained on chromed wool. On silk colours of good fastness to water and washing are produced.

*Jet black G*, another brand of the same colouring matter, dyes a dead black shade.

**SULPHONE CYANIN BLACK B, 2 B** (Bayer).

Brown powder; aqueous solution, dark violet; HCl, greenish-black precipitate; NaOH, soluble dark precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, dark violet; on diluting, greenish-black precipitate.

*Application.*—Wool is dyed with the addition of 2 to 3 per cent. acetic acid, and 10 to 20 per cent. Glaubersalt, the bath being exhausted with 1 to 2 per cent. acetic acid, or smaller quantities of sulphuric acid. Sulphone cyanin black dyes fine shades of black of excellent fastness to light, and very good fastness to milling, acids, and alkalis; they also resist light and steaming. They are therefore used for yarns and piece goods, especially for knitting yarns, and also for loose wool and shoddy. Sulphone cyanin black also dyes well in a neutral bath, and is therefore used for shading the wool in single-bath dyeing.

Silk is best dyed with the addition of acetic acid, the bath being exhausted with a small quantity of sulphuric acid.

**SULPHONE BLACK 3 B, 4 B T, G, R** (Bayer) are dyestuffs of similar properties, which are applied in the same way as Sulphone cyanin black, but do not possess quite the same fastness to light and milling.

**WOOL BLACK** (Berlin, B.A.S.F.).

Aminoazobenzene disulphonic acid—paratolybetanaphthylamine.

Blue-black powder; aqueous solution, blue-violet; HCl, red-violet precipitate; NaOH, soluble violet precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, blue; on diluting, dark red-violet precipitate.

Wool black is decomposed on prolonged boiling with dilute sulphuric acid, forming aminoazobenzene disulphonic acid and tolunaphthazine (*O. N. Witt*).

*Application.*—Wool black is used, as indicated by its name, for wool dyeing. As it is decomposed on boiling with dilute acid, it should always be dyed with the addition of sodium bisulphate, not with sulphuric acid. Enter warm and bring to the boiling point; boil for a long time, turning frequently, since the colour is liable to dye uneven at high temperatures; 4 per cent. of Wool black produces a blue-violet, 8 to 10 per cent. a black shade on wool, which can be toned with other acid dyestuffs. The shade is fairly fast to light, less fast to milling, and not sensitive to dilute acids or alkalis.

**WOOL BLACK 4 B, 6 B** (Berlin). **PALATINE BLACK 4 B, &c.** (B.A.S.F.).

Under the name of Wool black or Palatine black various brands of acid blacks are brought into commerce, which are said to be produced by the

action of (diazotised) sulphanilic acid and alpha-naphthylamine on 1 : 8 : 4 aminonaphthol sulphonic S.\*

Brown powder; aqueous solution, dark blue; HCl, dark precipitate; NaOH, blue; solution in  $H_2SO_4$ , blue; on diluting, dark precipitate.

*Application.*—These blacks are dyed on wool like the other acid blacks; it is best to begin with the addition of Glaubersalt and acetic acid, and to exhaust the bath with sodium bisulphate and sulphuric acid, or to dye straight with Glaubersalt and bisulphate or sulphuric acid. The various brands dye all kinds of bluish and reddish-black and jet-black on wool, which are fairly fast to light and washing and good to acids and alkalies. Wool black 4 B and 6 B and Palatine black 4 B dye also in a neutral bath, and are useful for shading the wool in dyeing unions by the single-bath method. Palatine black S and SS and Wool black 6 B W, 4 B W, and W do not stain white cotton shots when dyed in a strongly acid bath. Wool black 6 B, or, better still, Wool black G R, dyes silk in a boiled-off liquor bath acidulated with sulphuric, or in a bath without boiled-off liquor, but with the addition of acetic acid. Wool black G R, which materially differs from the other brands and is considerably faster to light, is also very useful for dyeing mixed fabrics of wool and silk.

**WOOL JET BLACK 2 B, 3 B** (Berlin) are similar to the preceding, and dye very deep shades of black.

**NEROL** (Berlin).

Brown powder; aqueous solution, black-violet; HCl, black precipitate; NaOH, little change; solution in  $H_2SO_4$ , blue-black; on diluting, blue-black precipitate.

*Application.*—Nerol comes into the market in various brands, such as Nerol B, B B, and Nerol blue-black. It is best dyed in a feebly acid bath with the addition of 10 to 20 per cent. Glaubersalt and 3 per cent. acetic acid. Enter into the boiling-hot bath and dye gently, boiling for one hour; then exhaust the bath by adding 2 to 3 per cent. more acetic acid. With yarns which have not been scoured, begin without acid and exhaust, after  $\frac{1}{2}$  or  $\frac{3}{4}$  hour's working at the boil, by adding 3 to 5 per cent. acetic acid. It is well to purify calcareous water by boiling with about 1 oz. of oxalic acid for 250 gallons of water and removing the scum of calcium oxalate forming on the surface of the liquor. Nerol is distinguished by excellent fastness to washing, and is used for yarns and slubbing, especially for knitting yarns. It possesses good fastness to acids and alkalies, but it is not very fast to light.

**BIEBRICH PATENT BLACK R O, B O, 3 B O, and 6 B O** (Kalle).

These are secondary disazo-colouring matters with Clève's naphthylamine sulphonic acids and naphthol sulphonic acids.

The "B O" brand shows the following reactions:—Black-brown powder; aqueous solution, dark violet; HCl, little change; NaOH, blue; solution in  $H_2SO_4$ , dark greenish-blue; on diluting, dark violet.

*Application.*—Same as Naphthol black. The "R O" brand yields, with 8 to 10 per cent. colour, a fairly reddish, the other brands more bluish-blacks on wool, which possess very good fastness to light, acids, and alkalies, and are moderately fast to washing.

**BIEBRICH PATENT BLACK A N, 4 A N, 6 A N, and 4 B N** (Kalle).

These dyestuffs contain aromatic amines instead of the naphthol sulphonic acids of the preceding brands. Black-brown powder; aqueous solution, dark violet; HCl, soluble violet precipitate; NaOH, makes the solution bluer; solution in  $H_2SO_4$ , dark greenish-blue; on diluting, dark precipitate.

*Application.*—These brands are dyed on wool with the addition of 10 per cent. Glaubersalt and 5 per cent. acetic acid, the bath being exhausted after about three-quarters of an hour's boiling by the addition of some sulphuric

\* *Sammel-Ausstellung der deutschen chemischen Industrie*, pp. 58 and 74.

acid or sodium bisulphate. The "4 B N" brand is decomposed on prolonged boiling in a bath containing much mineral acid, whereas the other brands are more stable, and can be dyed with sulphuric acid without the addition of acetic acid. The various brands yield good blacks fairly fast to light and washing, and not sensitive to acids or alkalies.

In addition to the preceding, a great number of acid blacks are found in commerce which more or less resemble the preceding blacks, and especially the oldest and typical acid blacks—*i.e.*, Naphthol black and Naphthylamine black. Of these may be mentioned :—

**PHENYLAMINE BLACK** (Bayer).  
**NAPHTHALENE ACID BLACK** (Bayer).  
**AMIDONAPHTHOL BLACK** (M.L.B.).  
**AMIDO ACID BLACK** (Berlin).  
**NAPHTHALENE BLACK** (Holliday).  
**ACID BLACK** (Holliday, Sandoz, &c.).  
**WOOL BLACK** (Levinstein).  
**BENZYL BLACK** (Ch. Ind. Basle).

#### **AZO-ACID BLACK (M.L.B.).**

This name refers to various mixtures for the production of very fine black shades, which mixtures are prepared very ingeniously, and possess such good levelling properties that they are of excellent service and find much application, especially in piece dyeing.

*Azo-acid Black S B L Extra* and *T L Extra*.—Brown powder; aqueous solution, dark violet; HCl, yellowish-red solution; NaOH, redder solution and soluble precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, red; on dilution, red.

*Application*.—The Azo-acid blacks are of excellent service in wool dyeing for piece goods, which require a short treatment in a distinctly acid bath in order to preserve the good qualities of the wool fibre and to avoid the formation of crimps and creases, especially for cashmere and mohair goods, cheviots, &c., and they may also serve for yarns. They are dyed like the easily levelling colours by commencing at the boil with the addition of 5 to 6 per cent. sulphuric acid and 20 per cent. Glaubersalt and boiling one hour. The black is fairly fast to light, moderately fast to washing, and withstands the action of acids, alkalies, stoving, and steaming. Cotton shots are not stained.

Blacks of a similar character are :—

**CASHMERE BLACK** (Bayer).  
**ETHYL BLACK** (B.A.S.F.).  
**AZO-MERINO BLACK** (Cassella).  
**AZO-PATENT BLACK** (Kalle).

## MORDANT-COLOURS.

### Artificial Dyestuffs which are fixed on the Textile Fibres with the aid of Metallic Mordants.

This chapter comprises a great variety of artificial dyestuffs which differ from the preceding colouring matters by the common property of dyeing the vegetable and animal fibres in conjunction with metallic mordants only. The most important of these dyestuffs, Alizarin, is also met with in the vegetable kingdom, and has been mentioned under "madder" in the chapter on the natural dyestuffs. It is distinguished by the property of yielding with different mordants different colours, which are characterised by extraordinary fastness to light, soap, milling, and other influences.

Several derivatives of Alizarin are applied in dyeing in the same way as Alizarin, and are distinguished by a similar resistance to colour-destroying

agents. These colouring matters, like Alizarin orange, Alizarin blue, or Anthracene brown, have been justly called "Alizarin colours"; but the name has been extended to several dyestuffs which are not at all chemically related to Alizarin—*e.g.*, Alizarin yellow A or C and Alizarin black—and only deserve the name because they are dyed by the same methods as the true Alizarin colours and can be dyed along with them in one bath. Later, however, a considerable number of dyestuffs have been introduced which share the property of dyeing on metallic mordants with the Alizarins (and are, as a rule, also very fast to the various agents). It does not appear appropriate to name all these colours "Alizarin colours," nor to separate the new additions from the older products, since they are very similar in their application and are frequently mixed in the dye-bath; hence we follow the recommendation of R. Nietzki,\* and classify all these dyestuffs as "mordant-colours." The common characteristic property of these dyestuffs is their ability to form insoluble colour-lakes with metallic oxides, which can be fixed on the textile fibres; but except for this property they differ greatly. Some cannot be dyed at all without mordants and cannot be considered as true colours, but as colouring principles which yield the coloured body only in combination with metallic oxides. Other colouring matters are more or less capable of dyeing the textile fibres without mordants—*e.g.*, Alizarin blue, Alizarin cyanin, Anthracene blue, &c. But this difference in behaviour seems to be unsuitable as a basis for a division into several groups. Hence, the grouping which will be adopted here is that depending on their origin, not on the distinguishing character, of the different mordant-colours.

- (a) *Alizarins.*
- (b) *Derivatives of Pyrogallol.*
- (c) *Various Phenolic Compounds* (Alizarin black S, &c.)
- (d) *Quinone-Oximes or Nitroso-compounds.*

The first group, comprising the Alizarins, contains the double ketone group  $\left\{ \begin{array}{l} \text{CO} \\ \text{CO} \end{array} \right\}$  as chromophor, and as auxochromous groups two hydroxyls in ortho position to each other, and one of them in ortho position to one of the groups CO. (See *Alizarin.*)

The second group consists of derivatives of pyrogallol (or gallic acid), they also contain two or more hydroxyls in ortho position to each other, and presumably one of them also in ortho position to the chromophor. Coerulein may also be numbered among the members of this group.

The third group consists of several substances which have little in common, and the chemical reactions which take place in dyeing with them are also different.

The fourth group is formed by various quinone-oximes or nitroso-compounds of analogous constitution. These substances differ chemically and tinctorially from the preceding colours, and we refer to the paragraph describing them specially.

The mordant-colours are used in the dyeing and printing of cotton, linen, wool, and silk, and are used in considerable quantities on account of the great fastness they possess to soaping and milling. As a rule, they are very fast to light and resist well most of the other agents, such as sulphur dioxide, chlorine, acids, or alkalies; in short, they belong to the fastest colours known.

The acid chrome colours (with the exception of the derivatives of Alizarin)—*i.e.*, the dyestuffs which usually are dyed in acid baths and fixed by *subsequent* chroming—will be discussed under a separate heading in the following chapter.

**Methods of Dyeing with the Mordant-Colours.**—The dyeing with the

\* *Journ. Soc. Dyers and Col.*, 1889. v. 161.

mordant-colours takes place, as a rule, in two phases:—(1) *Mordanting*; (2) *Dyeing (mordanting and dyeing method)*. Both operations may, in some cases, be done together in one bath by the *single-bath method*. Sometimes their order is inverted by first dyeing or “*stuffing*,” and subsequently fixing or “*saddening*” with the mordant (*Dyeing and saddening method*). More recently a great number of dyestuffs of distinctly acid character have been discovered which dye well in an acid-bath, and are also developed or fixed by subsequent mordanting, principally with bichromates or chromium salts (*one-bath or acid chroming method*). See also the next chapter, *Acid chrome colours*.

The various sesquioxides, principally those of aluminium, chromium, and iron, and, in addition, stannous and stannic oxide, are used as mordants; the other oxides are of minor importance. Chromic oxide is the mordant employed with the greatest number of these colours, while aluminium oxide yields the most brilliant shades, for example, “Turkey-red.” The principal mordant for the nitroso-compounds is ferric oxide; for other colours it is not frequently used, except for the production of very fast shades of violet with the aid of Alizarin on cotton.

Most of the mordant-colours can be mixed and dyed from the same bath, provided that they are fixed by the same mordant; colours requiring different mordants cannot be used with advantage for the production of mixed shades in one bath.

The colour-lakes frequently behave as mordants towards the basic colours, which latter are sometimes used to brighten or to shade a mordant-colour, either by adding the basic colour to the dye-bath or by topping afterwards.

Such of the mordant-colours as are readily soluble in water and sold in the form of powders, are added to the dye-bath in the dissolved state. They require 20 to 50 times their own weight of water; the solutions are filtered before being used. With the exception of the bisulphite compounds, they may be dissolved in boiling water. The latter, however, are decomposed by hot water, so that the water should be cold, or, at most, lukewarm. Many of the mordant-colours are sold as sparingly soluble pastes; these are mixed with some water and passed through a fine sieve into the dye bath; they are thus in a state of fine division and gradually dissolve in the dye-liquor. These pastes require care in storing; they should be kept in well-covered casks in a place where they are protected from frost and not liable to dry up; if not perfectly closed the casks should be covered with a damp cloth (which has been saturated with glycerin). Before taking out any paste from a cask it should be well stirred up with a wooden stirrer until the whole is of uniform consistency.

The paste loses in colouring power if it dries up, since it thereby becomes less soluble in the dye-bath. The best method of restoring its former quality is to dissolve the substance in caustic soda, precipitate the colouring matter with a slight excess of sulphuric acid, wash the precipitate with water, and dilute the resulting paste with a sufficient quantity of water.

**Dyeing of Cotton with the Mordant-Colours.**—Cotton is always dyed with these products by the separate “mordanting and dyeing method.” Aluminium, chromium, and iron mordants are principally used; their application has been described in the chapter on mordants (Part V.). Some special methods, notably the production of Turkey-red, will be described with the dyestuffs.

*Dyeing on Aluminium Mordants* (see p. 233).—These mordants are used for Alizarin, Alizarin orange, Alizarin maroon, Alizarin bordeaux, Anthracene brown, and Coerulein. The methods of dyeing are described in connection with the dyestuffs themselves.

**1st Operation—Oil Preparing.**—The washed goods are hydro-extracted, but not dried, and then worked in a bath containing 10 to 20 kgs. (lbs.) of

neutralised Turkey-red oil (50 per cent.) for every 100 litres (10 galls.) of water. When thoroughly saturated with the liquor they are evenly wrung out.

*2nd Operation—Stoving.*—The oiled goods are dried at temperatures ranging from 40° to 60°. Frequently the oiled goods are steamed under a pressure of 8 lbs. for sixty to ninety minutes, but this is not essential.

The compounds constituting the Turkey-red oil are decomposed by the operations of oiling, drying, and steaming, ammonium or sodium sulphate and various organic acids being formed, which consist of products of the oxidation and polymerisation of ricinoleic acid, &c.

*3rd Operation—Aluming.*—The goods are worked until well saturated in a warm bath (40° to 45° C.) of red liquor (10° Tw.), or of basic aluminium sulphate (10° Tw.), well wrung out and dried at 40° to 50°.

For the production of bright and intense colours the operations of oiling and drying and subsequent aluming are repeated once or twice.

*4th Operation—Chalking.*—The material is worked in a weak alkaline bath for the purpose of purifying it from an excess of oil and obtaining a more complete precipitation of the alumina which has been absorbed by the fibre during the aluming. A chalk bath is generally employed for this purpose (*chalking*). Brighter colours are said to be produced when phosphate of soda or ammonium carbonate are employed as fixing agents. Arsenate of soda gives still brighter colours than the phosphate. The cotton is worked for thirty minutes at 30° to 40° in a bath containing  $\frac{1}{2}$  kg. (lb.) of ground chalk per 100 litres (10 galls.) of water, then thoroughly washed and dyed without drying.

*5th Operation—Dyeing.*—Moderately hard water (4° to 10° of hardness), free from iron, is required, and the dyeing is best carried out in wooden vats heated by steam-pipes made of lead or tinned iron.

The whole quantity of dyestuff is added to the bath, and the wet material is entered at not more than 25° and worked for twenty minutes without heating. The bath is then heated to the boil within half an hour, and boiled one hour whilst continually working the cotton, which is then wrung and dried.

This process is a simplified form of the Alizarin-red process, and yields very good colours. Alizarin itself by the Alizarin-red process indeed gives finer and brighter reds.

Tannic acid, instead of Turkey-red oil, may be used for preparing the colours coming out less bright. The cotton is worked for some time in a hot bath of 20 to 25 per cent. sumach leaves (on the weight of the goods) and allowed to steep overnight, then wrung and directly entered into a bath of basic aluminium sulphate (10° Tw.); after turning for some time, it is again allowed to steep overnight, and, on the third day, it is sharply wrung and thoroughly rinsed in calcareous water. Calcareous water is also used for dyeing (with the exception of Coerulein), or a quarter of the weight of the dyestuff of calcium acetate dissolved in water is added to the dye-liquor.

Regarding the mordanting with aluminate of soda, see p. 595.

Pale shades may be dyed by the one-dip method. Prepare the bath with  $\frac{1}{2}$  to 3 per cent. dyestuff and 3 per cent. alum, turn, without heating, for fifteen minutes, heat gradually to the boil within forty-five minutes, boil one hour, rinse, and soap ten minutes with 2 kgs. (2 lbs.) soap per 1,000 litres (100 galls.).

*Dyeing on Chromium Mordants* (see p. 251).—The lack of a thoroughly satisfactory mordant, especially for yarn dyeing, has restricted to some extent the fixing of these colours on cotton by chromium, and the application of the mordant colours to cotton, especially to loose cotton and cotton yarn, is not very extensive.

It is not essential that the goods should be prepared with oil before mordanting; but the oil is a valuable fixing agent for the mordant, and, in addition, it gives a better appearance and greater fastness to the colour. Saturating the cotton once with oil (1 volume of neutralised Turkey-red oil (50 per cent.) diluted with 9 volumes of water) and subsequent drying, is sufficient. After the oiling, if necessary, impregnating with tannin—for instance, steeping in a hot solution of 1 part of sumach extract (53° Tw.) in 100 of water for twelve hours—follows, in some cases. The methods for mordanting cotton with chromic oxide have been described in the chapter on mordants; for yarn in hanks, basic chromium chloride, chromium acetate, and chromium mordant G A I. are the most suitable; for loose cotton, cops, or piece goods, in addition to these Koechlin's alkaline chrome mordant, and chromium mordant G A II. are applicable; Koechlin's mordant appears to be the best which has been recommended as yet. The method of producing a double chromium-zinc mordant with sodium zincate (p. 253) may also be used. With these alkaline mordants, however, a previous oiling is useless, the oil being stripped in the alkaline mordanting liquor. If it is desired to use a mixed aluminium and chromium mordant, it is best to fix first the necessary quantity of chromic oxide, and subsequently the alumina; the latter being fixed more easily than the former.

The mordanted goods are well washed in water to remove any loosely adhering mordant, which might cause the ultimate colour to rub and smear off. The goods are dyed immediately without drying.

The water is slightly acidulated by the addition of acetic acid; in the case of soft water, 1 part of acid is added for 1,000 parts of water, but for alkaline water more is used; a great excess of acid is injurious. Frequently some Turkey-red oil (2 parts of oil for 1,000 parts of water) is added to give the colour brightness. The colour is added to the dye-liquor, the goods are introduced into the cold bath, the temperature being raised in about one hour to the boiling point, and maintained thus for one to two hours. After the dyeing the goods are soaped at 60° or at the boil, rinsed in water, and dried.

Pale shades, as with alumina-mordants, may be dyed in one bath, the alum being replaced by an equal amount of chromium acetate, 1.16 specific gravity (32° Tw.).

*Dyeing on Iron, Tin, and other Mordants.*—The general application of these mordants has been given in the chapter on mordants. They are used in special cases only, and their employment will be described in connection with the dyestuffs for which they are required. The iron mordants are important for Alizarin purple and for the fixation of the nitroso-compounds. For the latter purpose nickel and cobalt salts also may be used in calico-printing.

Jute is not dyed with the mordant-colours, since the process of applying them is too expensive for this material.

*Dyeing of Wool with the Mordant-Colours.*—The use of natural mordant dyestuffs—*e.g.*, logwood, fustic, or madder—in wool dyeing dates from a very early period, and the employment of the principal wool-mordant—*viz.*, potassium bichromate—was introduced in the early part of the last century. The application of artificial mordant-colours in wool dyeing, however, only became general towards the end of last century. J. J. Hummel directed, in an admirable paper read in 1884 before the Society of Dyers and Colourists,\* the attention of wool dyers to the valuable properties of the Alizarin dyestuffs, and it is largely owing to his endeavours that the artificial mordant-colours have so rapidly found a general application in British dye-houses. The merits of the mordant-colours, especially of the true Alizarins, consist (1) in their extraordinary fastness to air and light, to dilute acids and alkalies,

\* *Journ. Soc. Dyers and Col.*, 1884-85, p. 11.



to milling, scouring, carbonising, and stoving—the smearing-off, or rubbing, which was formerly very objectionable, has been overcome to a great extent (see below); (2) in the fact that the wool does not lose its softness and spinning properties; in this respect the artificial mordant-colours are, as a rule, preferable to the wood-colours, which are mostly dyed on iron mordants.

An important factor for the successful dyeing of wool with these colours is the thorough purification of the fibre from fatty and greasy matters. Unless these are removed, they form with the mordants sticky soaps which loosely adhere to the wool and attract dyestuff; but as they form no intimate combination with the fibre, they are always disposed to rub off, and to soil other yarns they come in contact with in milling. It is most essential that the loose wool should be thoroughly scoured before it is spun, since it is almost impossible to remove “yolk” from the yarn; the difficulties frequently met with in yarn dyeing are often due to the fact that the wool from which it is spun has not been sufficiently scoured. In addition, yarns or pieces should be very well washed before dyeing.

*Mordanting.*—The same metallic mordants as are used on cotton are also used on wool for dyeing with the mordant colours—viz., aluminium, chromium, iron, and tin, in conjunction with, or without, calcium; all of these are employed more or less for Alizarin, but chiefly aluminium and chromium, especially the latter. Most of the other dyestuffs are fixed on chromium mordants only. The form, however, in which these metals are used in wool dyeing is different from that of those used for cotton, and no olive oil or Turkey-red oil is employed in wool dyeing.

The artificial mordant dyestuffs may be dyed together in the same dye-bath, and also in combination with logwood, fustic, &c. They may be saddened in the latter case with copperas or blue vitriol, and may be shaded by topping with acid colours, such as Patent blue A, Brilliant milling green, Cloth red, Milling yellow, or with levelling colours like Azo-carmin, Azo-fuchsine, Tartrazin, Flavazin, Fast light yellow 3 G, Patent blue, &c.

*Dyeing on Aluminium Mordant* (see p. 236).—Only the several Alizarin reds, Alizarin maroon, and Alizarin orange are fixed on wool with the aid of aluminium (see pp. 597, 601, 606, and 607).

*Dyeing on Chromium Mordants* (see p. 255).

(a) *Mordanting and Dyeing Method.*—The method most generally applied is boiling the wool with potassium bichromate (or sodium bichromate), with or without the addition of sulphuric acid or other assistants. The best results are obtained by mordanting with 3 per cent. of bichromate and 2½ per cent. of tartar; but lactic acid, formic acid, &c., are also very useful, and find much application.

The well-scoured and wetted-out wool is boiled for one hour, and in some cases even longer, in the mordanting liquor containing the required amount of bichromate, with or without sulphuric acid or tartar. About 2 to 4 per cent. of chromium fluoride, with half its weight of oxalic acid, may in some cases be used with advantage in place of bichromate (p. 255). The wool when taken out of the mordanting bath is well hydro-extracted, in order to prevent unevenness (dark lists, &c., caused by the excess of liquor collecting in the lower or hanging parts of the goods), and allowed to lie overnight, and next day it is well washed in water and dyed. Rinsing the wool in a dilute solution of sodium bisulphite (see p. 256) before the washing is beneficial in some cases, in others it is not advisable. The mordanted goods should be kept in the shade in order to prevent a partial change of the mordant by strong light which would result in subsequent uneven dyeing.

The dye-liquor is first prepared with acetic acid (30 per cent.) in the proportion of 1 part per 1,000 parts of water; the more alkaline the water the

more acetic acid is required; the water should have a distinctly acid reaction. A slight quantity of acetic seems to be beneficial to the formation of the colour-lake, while calcium salts are rather detrimental, but become innocuous by the addition of acetic acid. One part of acetic acid (30 per cent.) for 1,000 parts of water is required for about every 6 degrees of hardness. The colouring matter is dissolved or mixed with the acidified water taken from the dye-bath, and is added to the dye-bath (in the case of insoluble pastes, through a fine sieve). The material is entered into the dye-liquor at a low temperature, in order to ensure even and regular dyeing; the temperature should not be higher than 50° for dark shades, or 30° for light shades. After working some time in the bath the rest of the colour is gradually added. The temperature is slowly raised to boiling; but during the first hour 60° should not be exceeded—in dyeing with Obermaier's machine 50°—and the boiling point must not be reached before the dye-liquor is almost decolourised; one to one and a-half hours' boiling are required to develop and thoroughly fix the colour. Any further addition of colouring matter to the dye-bath, either to deepen or modify the shade, should only be made after cooling the dye-liquor down to 30° or 50° with cold water containing the requisite amount of acetic acid. The best fastness to milling is obtained with some colours—*e.g.*, Alizarin, Alizarin cyanine, and Anthracene blue—by a treatment after dyeing with  $\frac{1}{2}$  to 1 per cent. bichromate in a boiling bath for half an hour. After the dyeing is finished the wool is washed thoroughly.

To dye piece goods, yarns, and slubbing thoroughly and evenly, especially thick milled cloths, or lighter shades and "modes," the Badische Anilin- und Soda Fabrik recommends the following method of dyeing:—Add to 1,000 parts of water, heated to a temperature not above 40°, 3 parts (by volume) of ammonium acetate,\* and the required amount of dyestuff dissolved or mixed with warm water. Enter the goods and turn frequently, especially for the first fifteen minutes; raise in about forty-five minutes to boiling, and boil for thirty minutes more. For every 1,000 parts of dye-liquor add 3 parts of acetic acid (30 per cent.), divided into 3 parts; shut the steam off, lift the goods on each addition, and turn them frequently. Two hours more boiling fixes the colour thoroughly. For shading, the bath need not be cooled down, but the free acetic acid should be neutralised with ammonia; about 1 to 1 $\frac{1}{2}$  parts of ammonia per 1,000 parts of liquor are required; an excess must be avoided.

(b) *Single-bath Method.*—A number of mordant colours which are not chemically changed by the oxidising action of chromic acid, notably Alizarin, yield excellent shades in one bath, which are as full as those obtained by the mordanting and dyeing method, and almost equally fast to milling. Three per cent. of bichromate, and in some cases as much sulphuric acid, are used; in order to ensure even and regular dyeing, it is necessary to work for some time in the cold, then raise the temperature gradually to boiling, and keep at the boil for some time. Chromium fluoride is still better adapted for the "single-bath method" than bichrome, because it does not easily affect the colouring matters.

*One-bath or Acid-chroming Method.*—This method, which is chiefly used for azo-colouring matters, and for Alizarins in combination with the latter, will be described in the next chapter under the heading of "Acid chrome colours."

For *Dyeing with other Mordants*, see *Alizarin and Nitroso-compounds*.

*Stripping* Alizarins from wool is difficult owing to their good fixation and resistance to chemical agents. Boiling with alkaline liquids is of little effect. The best way is boiling with a strong solution of oxalic acid, 5 per cent., or even 10 per cent., oxalic acid being used, which quantity, however, is

\* The ammonium acetate is prepared by adding so much acetic acid to commercial ammonia water as will cause the mixture to give a very slightly acid reaction.

dangerous to the fibre. Sulphuric acid does not act quite as well. In some cases the colours become paler by boiling with a solution of 1 grm. stannous chloride and 1 grm. hydrochloric acid per litre ( $1\frac{1}{2}$  ozs. per 10 gallons), or by bleaching with potassium permanganate, or hydrogen peroxide, or sodium hydrosulphite (pp. 150 and 151), or sodium sulphonylate formaldehyde (p. 199), which treatments may be useful if it is desired to amend defects caused by bleeding of Alizarins.

**Dyeing of Silk with the Mordant-Colours.**—These colouring matters are not used very extensively on silk, because their fixation with the aid of mordants is much more expensive than that of the acid or basic dyestuffs, and the latter are, as a rule, fast enough for the requirements of silk dyeing, and yield more brilliant and purer shades. Besides, the mordant deposited in the fibre causes the silk to lose some of its lustre and pliability.

The silk is discharged, washed, and wrung out, and then mordanted with aluminium or chromium salts.

*Dyeing with Aluminium Mordants.*—See p. 238.

*Dyeing on Chromium Mordants.*—For darker shades the use of chromium mordants is preferable (see p. 258).

*Dyeing on Iron Mordant.*—Steep in basic nitrate of iron (p. 262) overnight, wring, wash, and soap in boiling soap solution (see also *Alizarin black*).

*Dyeing.*—The dye-bath should contain per 100 litres (galls.) 20 litres (galls.) of boiled-off liquor. The latter should be free from soda, and neither too old nor too slimy—*i.e.*, it should not contain too much gum. The liquor obtained from the second boiling-off is used with advantage. The amount of dye-liquor should be twenty to thirty times the weight of the silk.

For an aluminium mordant, the bath is neutralised with acetic acid; for a chromium mordant it is slightly acidified. The colour is added before the acid, the silk is entered as soon as the acid has been put into the bath, and worked cold for fifteen minutes; during forty-five minutes the bath is heated to boiling, and kept at this temperature for one hour more. The silk is then well washed in water and soaped for fifteen minutes in boiling soap solution 2 grms. per litre ( $\frac{1}{2}$  oz. per gall.); strong and prolonged soaping increases the brilliancy of the colours. Finally, it is worked for brightening in tepid water containing 25 grms. of acetic acid per litre (4 ozs. per gall.), and dried without washing.

The mordant- and dye-baths may be used continuously.

Pale shades may be dyed in the following way:—Prepare the bath with 3 per cent. alum and 2 per cent. oxalic acid, or 3 per cent. chromium acetate, 1.16 specific gravity (32° Tw.), and  $1\frac{1}{2}$  per cent. oxalic acid and the dyestuff, which is stirred to a thin paste with ten times its weight of water and added to the liquor through a fine sieve. Enter at 30°, turn one-quarter of an hour, heat to the boil within three-quarters of an hour, and boil one hour. Rinse, soap, and brighten as stated above.

On silk the mordant-colours are, as a rule, very fast to light, soap, or milling, if properly dyed. The affinity of the silk fibre, however, for the metallic mordants, especially for chromic oxide, is less distinct than that of wool; and the colours are not always fixed quite so fast on silk as on wool. Still the colours are much faster on silk than the acid or basic aniline colours, and deserve the attention of silk dyers.

## ALIZARIN AND DERIVATIVES OF ALIZARIN.

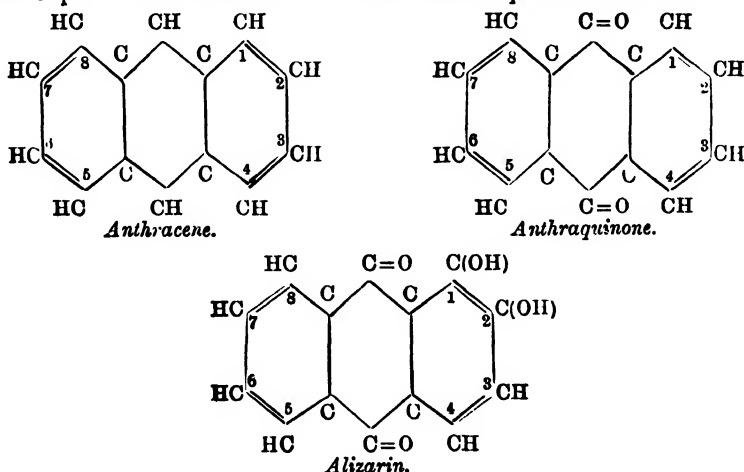
**History and Chemistry of Alizarin.**—According to the reports of Pliny, Dioscorides, and Strabo, madder-root was used for dyeing by the ancients. In eastern Europe this use has been continued ever since.

In western Europe madder disappeared from commerce for many centuries,

and, as late as 1507, its culture was re-introduced into Silesia, and at about the same time into the Netherlands. It was not until the eighteenth century that madder was cultivated in France, where, for some time, its production has been fostered by the Government.

The first systematic chemical examination of madder was made by Robiquet and Colin, who, in 1826, discovered therein two dyestuffs, Alizarin and Purpurin, and determined their exact composition. Further important investigations were made by Runge, Gaultier de Claubry and Persoz, Debus, Schunck and Römer, Rochleder, Strecker, and others, by whom our knowledge of these colouring matters has been promoted. But the results of their researches were conflicting, and even the exact composition of Alizarin and Purpurin became doubtful in the course of time. In 1868 two young chemists, C. Graebe and C. Liebermann,\* succeeded in clearing the darkness, and not merely discovered the constitution of both compounds, but prepared them from anthracene, a hydrocarbon which is present in coal-tar. As the fruit of their studies, the great Alizarin industry has been built up; the manufacture of other chemicals (*e.g.*, the bichromates and sulphuric anhydride) has been encouraged and stimulated, and their prices greatly reduced; and last, but not least, hundreds of thousands of acres which were used for the cultivation of madder have been made available for the production of the necessaries of life. Madder has almost completely disappeared from commerce because it could not compete with artificial Alizarin in price, purity, concentration, and uniform quality of the colouring substance. In wool dyeing it is still used to a slight extent because it dyes more level than the artificial product; but even here it owes its employment more to the antiquated demands of the consumer than to its intrinsic merits. On the other hand, effects, especially in calico-printing can be obtained with artificial Alizarin which could not be produced at all with madder or madder extracts, while its lower cost has brought about a saving in time and expense.

Alizarin, so called by Robiquet and Colin, after "Lizari," the trade name of the Levantine madder roots, is a derivative of the hydrocarbon anthracene ( $C_{14}H_{10}$ ), or rather of the double-ketone of the latter, anthraquinone ( $C_{14}H_8O_2$ ); Alizarin is dioxyanthraquinone ( $C_{14}H_8O_4 = C_{14}H_6O_2(OH)_2$ ). The following formulæ explain the constitutions of these three important bodies:—

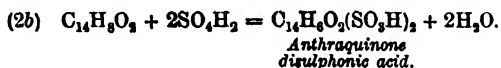
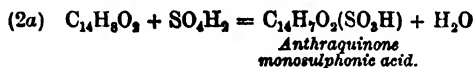
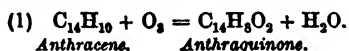


\* Recently the Perkin medal has been presented by the Society of Dyers and Colourists to Messrs. C. Graebe and C. Liebermann. See *Journ. Soc Dyers and Col.*, 1908, p. 130.

All true Alizarin colours are derivatives of this dioxyanthraquinone. The isomeric substances which do not contain the hydroxyls in the same position (in ortho position and next to one of the ketone groups, C = O) possess, according to the rule of Liebermann and Kostanecki as enunciated in 1885, no tinctorial properties. This rule had to be modified, as it was found that these substances, and even the monoxanthraquinones, possess the property of dyeing on metallic mordants, although but to a slight extent. But it may be stated that generally only those compounds are mordant dyestuffs of practical value which contain two hydroxyl groups in ortho position to each other, and one of them adjacent to the chromophorous group.

Alizarin is a phenolic substance, since it possesses hydroxyls connected with the benzene nucleus. It evinces much stronger acidity than phenol or the naphthols, and acts as a dibasic acid; it decomposes sodium acetate on continued boiling, forming sodium alizarate and acetic acid (see below). It forms with metallic oxides permanent compounds, the alizarates, which are (with the exception of those obtained with the alkalis) sparingly soluble or insoluble in water (colour lakes). (See also p. 573, *et seq.*)

The manufacture of Alizarin has been brought to a high state of perfection, almost the highest possible yield being realised. Anthracene is first oxidised with sodium bichromate and sulphuric acid, and the resulting anthraquinone is converted by very strong fuming sulphuric acid into sulphonic acids (mono-sulphonic, or alpha-disulphonic, or beta-disulphonic acid of anthraquinone). The sulphonic acids are converted into Alizarin or oxyalizarins by melting with caustic soda and a small amount of sodium chlorate; the melting is effected under high pressure in closed vessels.



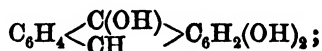
The product of the anthraquinone alpha-sulphonic acid is called "Flavopurpurin," while the name of that obtained from the anthraquinone beta-sulphonic acid is Anthrapurpurin (or Isopurpurin). Both are constituted thus:— $(\text{HO})\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{C}_6\text{H}_2(\text{OH})_2$ , while Purpurin, another oxyalizarin, is  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{C}_6\text{H}(\text{OH})_3$ .

In the preceding equations it will be noticed that the anthraquinone sulphonic acids yield products which contain each time one hydroxyl group more than the number of sulpho-groups originally present. Thus the monosulphonic acid gives Alizarin or dioxyanthraquinone; while from the disulphonic acids trioxanthraquinones are obtained. The hydrogen which appears in these equations would act on the product and diminish the yield; to prevent this, chlorate of potash or soda is added to the melt (invention of J. J. Koch). The sodium compounds of the product are decomposed by acids, and the dyestuff, which is precipitated in a very finely divided flocculent state, is well washed and ground to a homogeneous paste containing a fixed per-

centage of pure dyestuff; most of the commercial Alizarin now contains 20 per cent. of pure colouring matter.

The blue shade of Alizarin only consists chiefly of true Alizarin—i.e., that dioxyanthraquinone which can be obtained from madder. The yellow shade of Alizarin contains little Alizarin, but more Anthra- and Flavopurpurin; both are very similar to Alizarin, as also is Purpurin, which latter is formed by heating dry Alizarin dissolved in sulphuric acid with manganese peroxide or with arsenic acid.

Alizarin (dioxyanthraquinone) in the pure state forms a reddish-yellow powder, or long resplendent bright orange-red needles. It melts at 289° to 290° C. It is almost insoluble in cold and very slightly soluble in boiling water, but it dissolves readily, with a reddish-yellow colour, in hot alcohol, ether, benzene, glycerin, glacial acetic acid, and similar solvents. In caustic soda it dissolves with a blue-violet, in ammonia with a purple colour; from these solutions it is precipitated by hydrochloric and other acids. In concentrated sulphuric acid Alizarin dissolves with a brownish-red colour, and is precipitated from this solution by water without change; even hot sulphuric acid attacks Alizarin but little, but by fuming acid it is converted into a sulphonic acid. By oxidation with manganese peroxide or arsenic acid it yields Purpurin; when boiled with diluted nitric acid it gives phthalic and oxalic acids; fuming nitric acid forms nitropurpurin, and nitrous acid produces beta-nitroalizarin or Alizarin orange. Alkaline reducing agents decolourise it. It is converted by zinc dust and ammonia into colourless *desoxyalizarin*



other reducing agents produce different products.

Pure Alizarin is hardly attacked by chloride of lime, while Flavo- and Anthra-purpurin are strongly affected by this agent.

Alizarin is, generally, more stable than most other dyestuffs, and hence the colour possesses great fastness to light, and other agents.

Alizarin combines with metals forming salt-like compounds, either by combining in the free state with the hydroxides, or by the double decomposition of a soluble alizarate and a metallic salt. These lakes are but imperfectly known, as proved by the extended investigations of Liechti and Suida, which did not confirm the descriptions generally given. The lakes of the metals of the alkaline earths and of the heavy metals are insoluble, or sparingly soluble in water; the alkali- and ammonium-compounds of Alizarin are readily soluble in water.

Liechti and Suida\* have studied the calcium, aluminium, iron, and chromium lakes of Alizarin, and have so fully explained the facts as attested by long practical experience, that a *résumé* of their results may follow here with advantage.

(1) *Calcium Alizarate*,  $\text{C}_{14}\text{H}_6\text{O}_4\text{Ca}$ , is obtained by the double decomposition of calcium acetate or chloride and ammonium alizarate as a purplish-black, sparingly soluble, crystalline body which is easily decomposed by acids (even by oleic acid). Alizarin, when treated with water containing bicarbonate of calcium, forms a precipitate of calcium alizarate, but only after some hours standing. Normal calcium carbonate scarcely produces any change, even after prolonged boiling with Alizarin; but if aluminium hydrate is added a red lake is rapidly formed, carbon dioxide being evolved. Both acid and basic calcium alizarates are soluble in cold water and ammonia, but on heating the solutions normal calcium alizarate is rapidly formed. Normal calcium alizarate dissolves

\* *Journ. Soc. Dyers and Col.*, 1885, p. 271; 1886, pp. 102, 120, 131, 146.

in clear lime water, with a ruby-red colour; if the solution is boiled for a short time it is decolourised and a red-brown precipitate is thrown down, consisting of a basic calcium alizarate,  $C_{14}H_6O_4Ca + CaO$ .

(2) *Aluminium Alizarates*.—In the absence of calcium salts Alizarin in the free state does not, under any circumstances, combine with aluminium hydroxide.\* Normal aluminium alizarate,  $(C_{14}H_6O_4)_3Al_2$ , is best obtained by acting on the solution of ammoniacal Alizarin with aluminium sulphate. It forms a purplish-black mass, which is soluble in pure water and in alcohol, especially on heating, also in ammonia without being chemically changed. If heated with water under pressure to  $150^\circ C$ . it is converted into a basic aluminium alizarate. An excess of Alizarin prevents the precipitation of aluminium hydroxide from its salts by ammonia. The basic alizarates of aluminium are insoluble in water and alcohol, and the more basic they become the less soluble they are in ammonia.

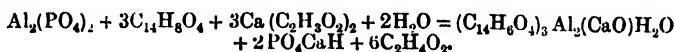
(3) *Aluminium-calcium Alizarates*.—No less than ten compound alizarates containing different proportions of aluminium and calcium were prepared and analysed. They are insoluble in water, but partially soluble in ammonia. The quantity of calcium which enters into combination to form the lake increases in proportion with increasing quantities of Alizarin employed; whereas, on the other hand, the quantity of Alizarin entering into the combination depends upon the lime present therein. Most fabrics dyed with Alizarin red contain an excess of aluminium relatively to the Alizarin and calcium; material mordanted with an unknown quantity of aluminium and subsequently dyed with Alizarin and calcium acetate—as is done in practice—takes up calcium in the proportion of one atom of calcium to three molecules of Alizarin. The most probable formula for the normal Alizarin red lake (before soaping) is  $(C_{14}H_6O_4)_3Al_2(CaO)_3H_2O$ . This lake is easily soluble in ammonia, and its ammoniacal solution can (like that of many others of these lakes) be mixed without change with Turkey-red oil. A lake of the composition  $(C_{14}H_6O_4)_4Al_2Ca$  was found to be partially soluble in ammonia and had a tendency to form the normal Alizarin red lake. By a dye-trial it was shown that the normal lake could take up more Alizarin; but this excess did not form an intimate combination and was removed by treatment with alkaline liquids (soaping). A lake,  $(C_{14}H_6O_4)_5Al_2Ca_2$ , described by Saget as being the fundamental compound of all Alizarin reds, is almost wholly soluble in water, and could not be produced under the conditions existing in the dye-bath; in place of it a basic lake is invariably formed. When treated with Turkey-red oil the aluminium calcium lakes absorb oxyfatty acid; the sulphuric acid liberated by the decomposition of the oil partially decomposes the lake, and free Alizarin as well as the sulphates of calcium and aluminium are formed. In all the ordinary Alizarin- and Turkey-reds the operation of soaping disturbs the ratio of the calcium to the aluminium, some of the latter being removed. At the same time the lake absorbs some fatty acid from the soap.

Alkaline solutions of the normal alizarate and of the basic aluminium alizarate,  $(C_{14}H_6O_4)_3(Al_2O_3H_3)_2$ , are not changed when mixed with solutions of sodium phosphate, Turkey-red oil, soap, &c.; but on neutralising the liquids magnificent red lakes are thrown down.

Since in mordanting on the large scale the pure aluminium hydrate is very seldom produced on the fibre, but is usually fixed by means of silicate, arsenate, or phosphate of soda, Liechti and Suida considered it necessary to investigate the action of at least one of the compounds thus obtained, and aluminium phosphate was selected. Normal aluminium phosphate,  $(PO_4)_2Al_2$ , prepared by precipitation and carefully washed, is not affected by Alizarin; if,

\* According to Möhlau and Steimmig (*Journ. Soc. Dyers and Col.*, 1904 p. 204), strontium, barium, and magnesium may take the place of calcium, but not with advantage.

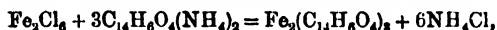
however, calcium acetate is added to the mixture, the formation of a lake ensues immediately. The filtrate has an acid reaction, and contains, besides acetic acid, a considerable quantity of phosphoric acid and calcium (most likely as acid calcium phosphate). This process is shown by the following equation:—



Aluminate of soda of the formula  $\text{Al}_2\text{O}_3, 2\text{Na}_2\text{O}$ , when acting on Alizarin in aqueous solution in the proportion of  $3\text{C}_{14}\text{H}_8\text{O}_4$  to  $1\text{Al}_2\text{O}_3$ , yields a red lake which easily dissolves in an excess of caustic soda or ammonia; aluminate of soda of the formula  $\text{Al}_2\text{O}_3, 3\text{Na}_2\text{O}$ , yields a fine red solution which is not affected by limewater. Turkey-red oil or soap can be added to the solution of the products of either aluminate with Alizarin, without producing a change; but on adding calcium acetate a precipitate is formed. A solution containing Alizarin, aluminate of soda, and calcium hydrate, printed on oiled material, gives a good steam-red.

(4) *Ferrous Alizarate*.—If solutions of ferrous sulphate and ammonium alizarate are mixed, a deep violet-black precipitate is at once produced which, after filtration and washing with water, is partly redissolved. This precipitate, when allowed to oxidise, probably forms a ferric ferrous alizarate,  $(\text{C}_{14}\text{H}_6\text{O}_4)_3\text{Fe}_2(\text{FeO})$ , which is constituted analogously to the above-described aluminium calcium alizarate; it forms, when dried, a violet-black powder, having a bronzy lustre. Ferrous alizarate, freshly made, is easily dissolved by ammonia with a violet-black colour. It may be mixed with Turkey-red oil in this solution without undergoing any change. The Alizarin here prevents the precipitation of ferrous or ferric hydrate by ammonia.

(5) *Ferric Alizarate*.—If a solution of ferric chloride is poured into one of ammonium alizarate, providing the weights correspond to the equation—



a brownish-black precipitate is formed, which is slightly soluble in pure water, very easily soluble in ammonia with a violet colour, and may be mixed without change in this solution with Turkey-red oil. From this precipitate Alizarin could be extracted by ether, while the residue contained one-half molecule of Alizarin less than is required by the formula  $\text{Fe}_2(\text{C}_{14}\text{H}_6\text{O}_4)_3$ . A still more basic ferric alizarate was obtained by boiling freshly-precipitated ferric hydrate with Alizarin suspended in water; the product contained about 2 molecules of Alizarin to 3 molecules of ferric oxide.

Cotton-cloth mordanted with ferric oxide yielded, when dyed with Alizarin in the absence of calcium compounds, only a very faint brownish-violet.

(6) *Ferric-calcium Alizarate*,  $(\text{C}_{14}\text{H}_6\text{O}_4)_3\text{Fe}_2(\text{CaO})\text{H}_2\text{O}$ .—Solutions of ferric chloride (1 mol.) containing different proportions (1, 2, or 3 mol.) of calcium acetate, were poured into solutions of ammonium alizarate (3 mol.). Also freshly-precipitated ferric hydrate (1 mol.) containing calcium acetate (1 mol.) was boiled with Alizarin (3 mol.) suspended in water. In each case, a product having the composition  $(\text{C}_{14}\text{H}_6\text{O}_4)_3\text{Fe}_2(\text{CaO})\text{H}_2\text{O}$  was obtained. The precipitate has a beautiful violet-black colour, and is partially soluble in ammonia. From the dye-trials executed in the same way and the analyses made, it further appears that this same product is the compound which forms the violet colour when Alizarin is dyed on iron-mordanted materials. While materials mordanted with iron and dyed with Alizarin in the absence of calcium gave only faint brownish-violet colours, those mordanted and dyed in the same way, except that the dye-bath contained increasing quantities (1, 2, or 3 mol.) of calcium acetate, yielded serviceable violet shades; the iron and



calcium were found to be present in the proportion of equal molecules, and this ratio was not even altered when their absolute amounts were diminished by soaping. Thus, it cannot be doubted that the composition of Alizarin violet is  $(C_{14}H_6O_4)_3Fe_2(CaO)H_2O$  and that it is analogous to Alizarin red  $(C_{14}H_6O_4)_3Al_2(CaO)H_2O$ .

(7) *Chromic Alizarates*.—The normal compound,  $(C_{14}H_6O_4)_3Cr_2$ , is obtained when chromium nitrate-acetate is treated with the corresponding amount of Alizarin and an excess of ammonia, and the resulting violet solution is boiled till completely neutral. Normal chromic alizarate is a purple-violet substance, insoluble in water, but readily soluble in ammonia with a violet colour; this solution can be mixed with Turkey-red oil without change. Liechti and Suida did not succeed in producing a basic chromic alizarate, but they obtained an acid chromic alizarate corresponding to the formula  $Cr_2(C_{14}H_6O_4)_3 + 3(C_{14}H_6O_4)$  as a purple-red substance, easily soluble in water and in ammonia.

(8) *Chromic-calcium Alizarate* was obtained by Liechti and Suida in a similar way as the normal chromic alizarate. If a solution of chromium nitrate-acetate, containing calcium acetate, is treated with ammonium alizarate, containing an excess of ammonia, a black-violet precipitate of calcium alizarate is formed. If the liquid, together with the precipitate, is boiled until the excess of ammonia has disappeared, the precipitate becomes more and more red-brown and the liquid colourless. The precipitate differs in composition according to the quantity of calcium acetate employed; if, for 3 molecules of Alizarin and 1 molecule of chromium salt, 1 molecule of calcium acetate were used, a product represented by the formula  $(C_{14}H_6O_4)_3Cr_2(CaO)H_2O$  was obtained; if, however, more calcium acetate (*i.e.*, 2 and 3 molecules respectively) were employed for the same amounts of Alizarin and chromium compounds, the ratio between Alizarin and chromium in the resulting lake seems to remain unchanged, while the quantity of calcium entering into combination increases, but in such a way that the calcium present is not entirely taken up. Thus when 3 molecules of calcium acetate were used the ratio of Alizarin, chromium, and calcium seemed to be 3 : 1 : 2. The precipitates are in each case insoluble in water, and the violet-brown colour approaches nearer to violet-black in proportion as the calcium is increased. These results were confirmed by dye-trials, which were made in the same way as those with ferric mordant. If the material was mordanted with chromium salt only and dyed without calcium being present, a faint puce only was obtained. If the experiment was regulated so that for 3 molecules of Alizarin and 1 molecule of chromium salt 1 or 2 or 3 molecules of calcium acetate were present in the colour obtained, the molecules of chromium and calcium occurred in the following proportions:—

For 1 molecule of calcium acetate used,	Cr : Ca = 1 : 0·48
“ 2 “ “ “ “	Cr : Ca = 1 : 0·56
“ 3 “ “ “ “	Cr : Ca = 1 : 1·04

Samples which contain a colour composed after the ratio  $3C_{14}H_6O_4 : Cr_2 : \frac{1}{2}Ca$  are of a darker puce shade than those produced in the absence of calcium, but they are not as dark as those containing a colour represented by the formula  $(C_{14}H_6O_4)_3Cr_2CaO, H_2O$ , which is obtained by using acetate of calcium in excess only. On soaping, the chromium-calcium-alizarin lake is much more altered in its composition than the corresponding iron lake.

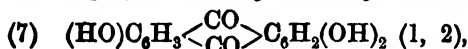
These facts are in complete harmony with all practical experience; they also explain why the presence of lime in Turkey-red dyeing is absolutely necessary; why, in dyeing with chromium mordants, the presence of calcium salts may be dispensed with to some extent; and why different amounts

of the latter give different results in dyeing with chrome- but not with alumina-mordant.

A. G. Perkin, in a study on phenolic colouring matters,\* has brought forward the opinion that in such compounds which contain but one keto group—*e.g.*, those of the flavone series—one hydroxyl only acts, although they may contain two or more hydroxyls, the various salts always possessing the same shade. If, however, the dyestuff contains two keto groups and two hydroxyls, as in the case of the Alizarins, various quinonoid salts of widely differing shades may be formed. It is accordingly suggested that the variety of shades met with among the Alizarin group is due either to alteration in the quinonoid form, or to the possibility of two such arrangements existing in the compound at the same time.

Alizarin S is the sodium monosulphonate of Alizarin.

Isopurpurin or Anthrapurpurin or *oxyisoanthraflavic acid*,



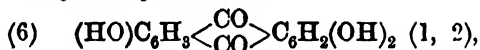
is obtained in the same way as Alizarin, anthraquinone beta-disulphonate of sodium being used instead of the monosulphonate. It closely resembles Alizarin.

Isopurpurin crystallises from hot alcohol as orange needles, which melt above 300° C. It is almost insoluble in water, but freely soluble in hot alcohol. It dissolves in caustic alkalies, in ammonia, and in sodium carbonate with a violet colour, which is redder than that obtained with Alizarin, but bluer than that from Flavopurpurin. Isopurpurin dissolves in sulphuric acid with a brown colour; water precipitates it from this solution without change.

Isopurpurin yields more yellowish shades than Alizarin, but less yellowish than Flavopurpurin.

Alizarin 2 S is the sodium monosulphonate of Isopurpurin.

Flavopurpurin or *oxyanthraflavic acid*,

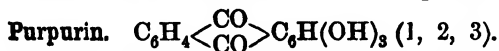


is isomeric with Isopurpurin and is obtained, like this substance, when anthraquinone alpha-disulphonic acid is melted with caustic soda by the Alizarin process. It closely resembles Alizarin and Isopurpurin.

Flavopurpurin forms yellow needles, which melt above 330° and can be sublimated; it is almost insoluble in water, but readily soluble in cold alcohol and in hot glacial acetic acid. It dissolves in caustic soda with a purple colour, which is redder than those of the analogous solutions of Alizarin and Isopurpurin; in ammonia and in sodium carbonate Flavopurpurin dissolves with a yellowish-red colour. The solution in sulphuric acid is red-violet; on diluting with water the dyestuff is precipitated without change.

The shades obtained with Flavopurpurin are yellower than those obtained with Alizarin and Isopurpurin.

Alizarin 3 S is the sodium monosulphonate of Flavopurpurin.



Purpurin was discovered by Robiquet and Colin along with Alizarin in the madder roots. It was the first oxyalizarin or trioxyanthraquinone discovered, and is isomeric with Isopurpurin and Flavopurpurin. Purpurin is not a product of the Alizarin melt, but can be obtained by oxidation of Alizarin. Purpurin forms red needles, which begin to sublimate at 150° and melt at 253°. In boiling water, in alcohol, and other solvents it dissolves with an

\* Journ. Soc. Chem. Industry, 1903, p. 605.

intensely yellow to reddish-yellow colour. Purpurin dissolves in caustic alkalies, ammonia, and carbonate of soda, with a purple colour, redder than Alizarin, Flavo- and Isopurpurin. The alkaline solution of Purpurin, when exposed to light and air for some time, is decolourised, the colouring matter being destroyed. Purpurin dissolves in sulphuric acid with a pink-red colour; water precipitates it again. The most characteristic property of Purpurin is that it dissolves in a boiling solution of alum with a yellowish-red colour and green fluorescence; the Purpurin-aluminium lake also has this property. Purpurin dyes a fiery red on aluminium mordant, which, however, is less permanent and more expensive than those obtained with the two isomeric Purpurins.

The distinguishing reactions of Alizarin and the three Purpurins are as follows:—

Name of dyestuff.	Solution in caustic soda.	Solution in sulphuric acid.	Point of sublimation.
Alizarin, . . .	Blue-violet.	Brownish-red.	Much below 160° C.
Isopurpurin, . .	Violet.	Brown.	at 160°
Flavopurpurin, .	Purplish-red.	Red-violet.	at 170°
Purpurin, . . .	Red.	Cherry-red.	at about 150°

In an alkaline solution of red prussiate, fibres dyed with lakes of Alizarin or Flavopurpurin or with the aluminium lake of Isopurpurin are not changed, while the iron lake of Isopurpurin and the lakes of Purpurin are destroyed.

#### COMMERCIAL ALIZARIN.

Alizarin is sold as a paste containing 20 per cent. of dry matter, representing nearly pure dyestuff, as a paste containing 40 per cent. of dry matter, and as a powder containing 80 per cent. and more. As to the storing of Alizarin in paste form, see p. 565. Two essentially different shades of Alizarin are distinguished, which are marked by the makers with different and contradictory letters, but which will be here referred to as Alizarin V or blue shade and Alizarin G or yellow shade (or for red).

(1) Alizarin V (violet) or *blue-shade Alizarin* is the purest commercial Alizarin; it contains small quantities of Iso- and Flavopurpurin in varying proportions, and in addition very small amounts of anthraquinone and oxyanthraquinone; the presence of these substances are proofs of the origin of Alizarin from anthraquinone, whilst the Alizarin from madder would contain Purpurin, and hence have the fluorescence characteristic of that substance.

Alizarin V forms an ochre-yellow paste (or powder). For the production of Alizarin pink the employment of Alizarin V is necessary to obtain a clear and delicate tint; a pure Alizarin violet on an iron mordant can also be produced with Alizarin V only (hence the name Alizarin V—i.e., “for violet”); Alizarin G yields on an iron mordant reddish or brownish shades.

(2) Alizarin G (i.e., “gelb” = yellow) or *yellow-shade Alizarin* or *Alizarin for red* is mainly a mixture of Iso- and Flavopurpurin containing also some Alizarin. The commercial product forms a brownish-yellow paste (or powder). Isopurpurin is more suitable for dyeing than Flavopurpurin because it resists the action of the clearing bath better; Flavopurpurin is preferable for printing, because it is more readily fixed by steaming. On the other hand, if strong clearing can be dispensed with, or if high-pressure steam is applied, either compound can be used equally well.

For the production of a fiery Alizarin red, Alizarin G is used, Flavopurpurin giving still more yellowish shades than Isopurpurin.

The methods for distinguishing the isomeric compounds have been already stated (pp. 577 and 578).

The value of the dyestuffs is best estimated by comparative dye-trials. They are frequently tested by determining the percentage of dry substance; but the latter is easily increased by adulterations. If the amount of dry substance is to be ascertained, the drying temperature should not rise above 100° C.; if it does, loss by sublimation may occur. A good product should not leave more than 1 per cent. of ash on ignition and should be completely soluble in caustic soda.

*Application of Alizarin V and G.*—The Alizarins—i.e., the colouring matter of commercial Alizarin—are adjective and polygenetic dyestuffs, since they are fixed exclusively with the aid of mordants, and produce with different mordants essentially different colours.\* They yield shades which are distinguished by brilliancy, fulness, and fastness; and are of great importance for the dyeing of the vegetable and animal fibres.

As madder was used for centuries as a dye for cotton wherever a fast red shade was required, so Alizarin is now in general use; but each year the quantity of Alizarin consumed in the dyeing and printing of Turkey-reds and Alizarin reds on cotton is many times greater than the largest annual production of pure colouring matter yet obtained from madder.

Fast shades of scarlet, prune, maroon, violet and black and numerous mixtures are produced both on cotton and on linen, with the aid of the various mordants, wherever fast colours are demanded.

The consumption of Alizarin in wool dyeing has also been considerable since dyers have learned to appreciate its valuable tinctorial properties and to overcome the difficulties accompanying its application (p. 567). More recently, however, it has lost ground, being frequently replaced by acid chrome colours.

Silk is not extensively dyed with Alizarin for the reasons given in the beginning of this chapter.

*Dyeing of Alizarin on Cotton.*—Aluminium, chromium, iron and tin salts are used, in conjunction with calcium salts, for the fixation of Alizarin on cotton. The most important is the aluminium-calcium mordant, which is used in various forms; the celebrated Turkey-reds and the Alizarin-reds are produced with it.

*Turkey-red (Adrianople Red; Indian Red).*—The art of producing a fiery and permanent red on cotton with the aid of madder roots, fatty oils (buffalo's or sheep's milk), and aluminium salts was known in the East Indies centuries ago, from whence it spread westward through Persia, Armenia, and Syria to Turkey and Greece. Since the middle of the eighteenth century the art of dyeing this brilliant red was brought by Greek dyers to Rouen, Lyons, and Languedoc in France, where several "Turkey-red" dye-works were founded. In 1765 a pamphlet, written by Le Pileur d'Apligny,† was published by the French Government, in which full instructions are given for producing Turkey-red. As a result of this publication the process became widely known and employed in Western Europe. The first Turkey-red dye-works in Great Britain were probably founded in Glasgow in the year 1790, in which district (Vale of Leven) the Turkey-red dyeing industry of that country is still chiefly located; Turkey-red is dyed also in large quantities in the vicinity of

\* F. Driessen has shown in a very valuable contribution (*Bull. de Mulhouse*, 1902, p. 180; *Journ. Soc. Dyers and Col.*, 1902, p. 190) that no Turkey-red is produced in the absence of alumina, although in some Asiatic processes no alumina mordant is used. Driessen found that *djirak*, the plant employed in India for this particular purpose, contains sufficient quantities of alumina, and he supposes the same to be the case with other plants used for dyeing this red.

† *Mémoire contenant le procédé de la teinture du coton rouge incarnat d'Adrianople sur le coton filé.*

Mulhouse (Alsacia), Elberfeld-Barmen (Prussia), and elsewhere. In Western Europe Turkey-red was at first exclusively dyed on cotton yarn; but in 1810 Koechlin of Mulhouse introduced it as a dye for woven fabrics.

The process as it came from the East was very lengthy, requiring as much as four months; but the time was much shortened prior to the discovery of Alizarin, some 125 years later; and now Turkey-red can be produced in three days, which is as fast to light as the colour obtained by the long process. No difference exists between the fastness of the red dyed with madder or with Alizarin. But the colour obtained by the long process is more resistant to chlorine, and slightly clearer than the red produced quickly with the aid of Turkey-red oil, probably on account of the incidental bleaching of the fibre by the sun during the prolonged and frequent exposures in the fields after the repeated oiling operations; and there are dyers in various parts of the world who still use the old method and obtain for the products correspondingly higher prices; but these form a very small part of the Turkey-red produced.

During the last quarter of the nineteenth century a revolution in Turkey-red dyeing has been caused by the substitution of Alizarin for madder, and by the introduction of new methods of oiling. Dyers willingly accepted the artificial dyestuff, since it was well adapted for application by the long established dyeing processes; but weavers at first complained that the yarns were too greasy and could not be sized well. Dyers, however, soon recognised the fact that the artificial dyestuff did not require such severe clearing with soap and soda as the natural products, and that the amount of oil in the preparation of the yarns could be diminished; thus this drawback was rapidly overcome, and as early as 1873 Alizarin had completely displaced madder in some of the principal dye-works of Switzerland, notwithstanding the high price at which Alizarin was then sold. This was principally due to the brighter shades that could be obtained and the shortening of the processes of oiling and brightening (Sansone).\*

In the old process lukewarm rancid olive oil is used. Under the name of "Steiner's process" a much shorter method of oiling the goods with very hot olive oil came into use. But olive oil has been replaced in most dye-houses altogether by new preparations of castor oil (or of olive oil), the so-called Turkey-red oils, with the aid of which products the oiling operations could be reduced in number and in time without too great a loss in fastness. Thus fine shades of New Turkey-red are obtained at relatively low prices and in a short time, which are exceedingly fast to light and soap, although inferior to the red obtained by the emulsion process. Finally, we may mention various processes of dyeing a red on cotton with the aid of Alizarin and aluminium mordants without any *previous* oiling of the goods, although an oiling follows the dyeing. These shades are not considered to be Turkey-reds; they are called *Alizarin reds* and are inferior in fastness and brilliancy to Turkey-red; still they belong to the fastest colours produced and are dyed in very great quantities, especially on cotton piece goods.

Turkey-red, as produced on the fibre, is a very complicated compound, the basis of which probably is the calcium aluminium lake,  $(\text{C}_{14}\text{H}_6\text{O}_4)_3\text{Al}_2, \text{CaO}, \text{H}_2\text{O}$ , described by Liechti and Suida (p. 574). The following series of operations serves for the production of Turkey-red:—

- (1) *Oiling* with a fatty oil (olive oil, castor oil, or Turkey-red oil).
- (2) *Sumaching*.
- (3) *Mordanting* or *Aluming*.
- (4) *Dyeing*.
- (5) *Clearing*.

\* *Journ. Soc. Dyers and Col.*, 1885, p. 203.

A considerable number of washings are absolutely necessary between these processes in order to obtain anything like a good red colour ; but the formation of the colour itself is independent of these.

(1a) *Oiling with Olive Oil*.—Oils of vegetable origin are exclusively used, olive oil being superior to all others. (In the East Indies the crushed castor-oil seeds are used.) The best kind of olive oil for this purpose is the rancid Gallipoli oil or emulsive oil (French, *huile tournante*) which has become rancid by the nitrogenous and extractive matter which it contains. It contains, owing to partial decomposition, more or less free fatty acids (oleic acid and others) as also free glycerin. This oil forms a milky emulsion with sodium carbonate, which emulsion may be partly a solution, and partly a mixture of the finely-divided undecomposed oil with the soap (formed by the free acid and sodium carbonate), free acid and possibly glycerin. This emulsified oil is absorbed by the fibre with special facility. The process of oiling consists in steeping the cotton material (yarn or piece goods) in the emulsion, and subsequently exposing the fibre saturated with the oil to the action of the open air (ageing), or (in Steiner's process) to an elevated temperature in ageing rooms. To increase the quantity of oil thus deposited and transformed in the fibre the oiling and exposing process is repeated several times.

By the exposure the oil is rendered insoluble so as to adhere permanently to the fibre. The chemical reaction effecting this change probably consists in a further decomposition of the olive oil into free acids and glycerin and in an oxidation and polymerisation of the liberated oleic acid under the influence of air, light, heat, moisture, and sodium carbonate. This has not been well established, but it is well known that oleic acid is very oxidisable and disposed to polymerise ; according to Camille Koechlin, 1 part of oleic acid absorbs 300 to 400 parts (by volume) of oxygen under the influence of light. The fact that when recently-oiled goods are piled up in heaps without being aired by turning, the temperature rises considerably, and may even reach spontaneous ignition, appears to favour the view that an oxidation takes place.

From the fibre which has been thus prepared and well washed, a substance can be extracted by solvents which does not contain any glycerin, part of which gives a soap with barium hydroxide, while another part is neutral and cannot be saponified. These compounds are probably the products of oxidation and polymerisation of oleic acid and possibly of the other components and admixtures of olive oil. The fibres which have been deprived of these substances do not yield a serviceable red with Alizarin, but a fair colour is obtained when cotton is impregnated with the extract and subsequently mordanted with alumina and dyed with Alizarin.

The oil as fixed in the fibres has probably a double effect :

(i.) It combines with and helps to fix the metallic mordant, as in the case of Turkey-red with aluminium and calcium, and in the very similar case of violet with iron and calcium ;

(ii.) It forms a colourless transparent varnish around the colour lake which protects the same from the influence of light, air, and chemical agencies, and, at the same time, increases the lustre and fastness of the shade. It may be assumed that in the more rapid processes of preparing the cotton sufficient time is not given for the formation of this varnish-like substance ; this would account for the inferior fastness of such kinds of Turkey-red.

(1b) *Oiling with Turkey-red Oil*.—The use of an olive oil which had been treated with sulphuric acid, as is now the case in the manufacture of Turkey-red oil, was recommended as early as 1834 by Runge in his work, *Farbenchemie* (chemistry of colours). During the seventies of last century Fritz Storck and Dr. Wuth discovered, almost at the same time, the preparation of Turkey-red

oil from castor oil, and by its use greatly simplified the process of Turkey-red dyeing.

The nature of Turkey-red oil has been discussed in Part V. (p. 175), and it has been stated that it contains compounds of certain organic acids with the radical of sulphuric acid, which represent either a sulphate (ester) or a sulphonic acid of ricinoleic acid. These compounds are rapidly decomposed under the influence of ageing and steaming, the sulphuric acid being separated from the organic acids and the latter being transformed into substances similar to those produced by the preparation of cotton with emulsive oil. The advantage of the Turkey-red oil over the emulsive oil is that it can be fixed in a short time by ageing, thereby allowing the laborious and lengthy exposure to the air to be dispensed with.

The cotton which has been prepared with oil (by either method) is now treated with warm water and then with caustic soda (steeping). By this operation the fibre is purified, while the oil which has been fixed on the material is not affected.

(2) *Sumaching*.—The cotton is usually saturated with a decoction of sumach after it has been impregnated with the oil. The object of this process is to introduce tannic acid into the fibre so as to render it capable of fixing, during the subsequent "aluming" operation, a larger quantity of alumina and of ultimately acquiring a fuller colour. It is uncertain whether the tannic acid enters at all into the ultimate colour lake or whether it forms a separate lake with the alizarate of aluminium and calcium. The sumaching operation is not absolutely necessary, since there is no decrease of fastness or of brilliancy of colour and no alteration of the shade if it is dispensed with. The sumaching, however, is considered by some dyers to give the colour a greater resistance towards the action of chlorine.

(3) *Aluming*.—By the process of mordanting with aluminium salts, one of the metallic mordants which is required for the formation of the red colour lake—namely, aluminium—is incorporated with the material. It is permanently fixed by the subsequent operations of ageing, washing, and chalking, while the acid of the aluminium salt is removed. Calcium, the other metallic mordant, need not be introduced into the fibre before dyeing.

Sometimes a small amount of stannous chloride or, better, stannous acetate is added to the mordanting bath to produce a more fiery shade; but what part the tin has in the formation of the colour lake is unknown. Some add the tin salt to the dye-bath or to the second clearing bath; but nothing definite can be said as to its mode of action.

(4) *Dyeing*.—The mordanted material is dyed in a bath which has been prepared with the required amount of Alizarin, and which must also contain a certain amount of lime salt to form the colour lake. If the water has great temporary hardness, it contains the required amount of lime salt in the form of calcium bicarbonate; but if it is very soft, some chalk or calcium acetate must be added. It has been shown by Liechti and Suida (see above) that Alizarin and aluminium do not combine in the absence of calcium compounds; but the addition of a calcium salt causes the rapid formation of a lake, which is probably constituted according to the formula  $(C_{14}H_6O_4)_3Al_2 \cdot CaO \cdot H_2O$ . Sometimes a stannous salt is added to the dye-bath, which may have the double effect of producing an Alizarin-tin lake and of reducing ferric oxide, thereby preventing the latter from forming part of the colour lake; the ferric oxide, which is easily introduced into the dye-liquor as an impurity, has a very dulling effect on Alizarin-red shades.

Alizarin and calcium are taken up by the fibre from the dye-bath; but the lake is not completely formed until the temperature is raised above 70°; if the goods have been dyed at a lower temperature, as is the case in the

sulphated oil process, they possess a reddish-orange colour when they are taken from the bath, and the red is developed by steaming only, which process completes the long chain of operations required for the formation of the colour-lake, provided that in the second clearing bath no further change is effected.

(5) *Clearing*.—The dyed goods are treated twice with hot solutions of soap. The first soaping merely removes a great amount of impurities which become attached to the fibre during the lengthy operations of oiling, mordanting, and dyeing. The utility of the addition of stannous chloride to the second soap bath is disputed. This salt makes the soap solution more neutral, sodium chloride and a stannous soap being formed. Possibly the stannous salt exerts a reducing action on the ferric compounds which may have been taken up during the preceding process and which would dull the shade, while the stannic oxide thereby formed enters the colour lake and renders the shade brighter and more fiery. It is contended, however, that stannous chloride cannot act in this way when added to the clearing bath, as the colour lake has already been formed, and that it should therefore be added to the mordanting liquor or to the dye-bath. According to another view, which is supported by Liechti's researches, a tin oleate is produced by the action of stannous chloride in the clearing bath, and is spread as a varnish over the fibre without entering into combination with the colour lake itself. Liechti has shown that 60 per cent. of the fatty acid of the soap employed may disappear and become fixed on the fibre (*Hummel*).

### TURKEY-RED DYEING PROCESSES.

I. *Old Process or Emulsion Process*.—The process which serves for the production of the very fastest Turkey-red on cotton-yarns is conducted in the following manner:—\*

*1st Operation—Boiling*.—The yarns are never bleached by chemicking (or treatment with chloride of lime solution), but simply freed from the naturally adhering fatty and resinous substances by "bowking"—i.e., boiling under pressure with alkaline liquors. The general method is to boil the yarn for four to five hours, under a pressure of 30 lbs., in a solution of caustic soda-lye of 1° Tw. Some use silicate or carbonate of soda or work in low-pressure kiers; in these cases the boiling has to be continued for six to eight hours. When the yarn has been thoroughly cleaned in this way it is washed well with water, hydro-extracted, and dried in a stove at 50° to 60°.

*2nd Operation—First Green Liquor*.—The yarn is passed into the so-called first green liquor, which is prepared by mixing rancid olive oil with sodium carbonate and sheep- or cow-dung. The most suitable olive oil is that which forms the most perfect and permanent emulsion with the smallest quantity of sodium carbonate. For 100 kgs. (100 lbs.) of yarn the bath is made up with 15 kgs. (15 lbs.) of emulsive oil, 1½ to 2 kgs. (lbs.) of dung, 200 litres (20 galls.) of water, and so much of a concentrated solution of sodium carbonate as will bring the liquor to a specific gravity of 2° Tw. In this bath the yarn is thoroughly saturated with the emulsive liquor, at a temperature of about 40°, for half a minute, and then wrung out evenly. This process, usually called *tramping*, is done by "tramping machines," which steep the single hanks into the liquors and often also wring out the hanks without much hand labour. Fig. 59 shows a tramping and wringing machine by D. Stewart & Co., Glasgow, which has superseded the hand process, and turns off ten hanks per minute. At one end of the machine two attendants place the hanks on revolving reels, R, which run in a little cistern, C, supplied with the tramping liquor; when saturated, the hank is placed on a pair of hooks, HH<sub>1</sub>, of which there are six

\* The description of this process is taken in the main from J. J. Hummel's work, *The Dyeing of Textile Fabrics*, p. 427.



such pairs carried on large discs, D, on either side of the machine. During the revolution of the discs, by a combination of rack and pinion, a twisting movement is imparted to the hank, thus wringing out the liquor, the strain being regulated by springs. Having traversed a fixed distance the hank becomes untwisted, while the pinion on the hook engages with another rack, and the hank is twisted in the opposite direction to be again untwisted and delivered from the hooks by a pair of arms, A A, fixed on a wyper shaft.

After being well prepared the hanks are thrown out into heaps for the night; on the following morning they are exposed to the open air until they feel dry; and, finally, they are placed in "stoves" heated to 60° C. for twelve hours (*stoving*). In some works which produce the very best kinds of Turkey-

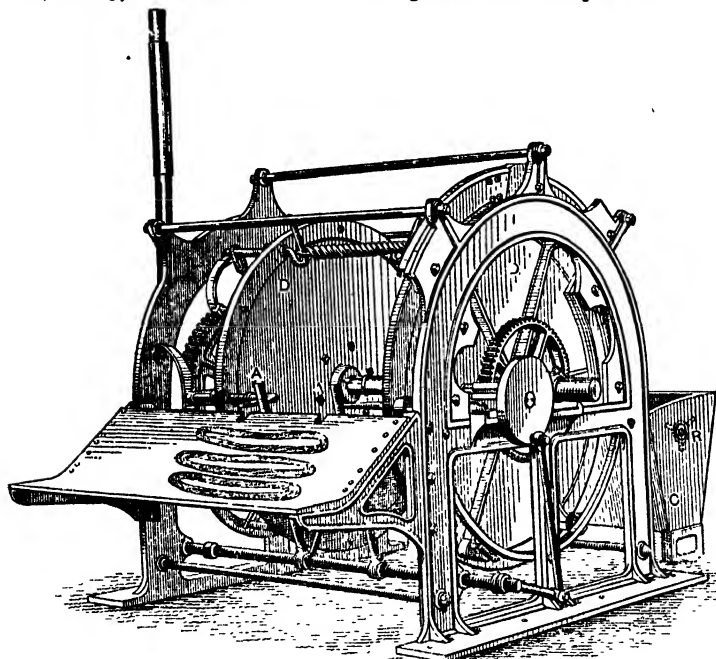


Fig. 59.—Tramping and wringing machine.

red, as regards fastness to alkalis and to chlorine, the yarns are exposed in the open air for three or more days, and then they need not be placed in the stoves; while at the present time they are frequently brought straight into the stoves after having been piled up overnight. In this last case the steam given off in large quantities during the drying must be allowed to escape, as its retention causes the fibres to be tendered.

During the prolonged exposure of the yarns in the open air the fibre is bleached by the sun, especially in the sunny Eastern Countries;\* the slightly greater brilliancy of the Turkey-reds which have been produced in the East is attributable to this action.

*3rd and 4th Operations—Second and Third Green Liquors.*—These consist of a second and third repetition of the second operation, the object being to increase the amount of oil in the fibre. The baths are prepared exactly as for the first green liquor, and the goods are steeped, exposed to the air, and stoved as before; but it is not necessary to pile them up to lie in heaps overnight.

\* P. Lukjanoff, *Journ. Soc. Dyers and Col.*, 1886, p. 29.

Some of the alkali which is used in preparing the bath is liberated by the chemical transformation of the oil in the fibre and dissolves, during the second and third treatment, in the green liquor which is absorbed by the yarn. The excess of this liquor, which is pressed out by the wringing of the hanks, if allowed to flow back into the tramping tank, would change the specific gravity of the bath, and as it is of importance that all the liquors should be maintained regularly of the same specific gravity, only the liquor which is expressed during the steeping in the first oil bath is allowed to run back into the tramping tank; that from the second and third oil baths is collected separately and used only after being reduced to its original specific gravity by dilution with water.

About 30 per cent. of oil of the weight of the yarn is used, but only a part of this is permanently fixed in the fibre.

*5th, 6th, 7th, and 8th Operations—First, Second, Third, and Fourth White Liquor Baths.*—The yarn has been impregnated with oil, and the latter transformed into such a state by the hanging and stoving operations that it is not readily stripped by weak alkaline liquors. A part of the absorbed oil, however, has not become insoluble or adheres superficially to the fibre. This oil is removed by repeated treatments with alkali in order to avoid the formation of the "surface" colour, which is always disposed to rub and smear off.

The goods are *tramped* for this purpose four times in solutions of sodium carbonate (2° Tw.), wrung out, hung up in the open air, and "stoved" as in the previous operations; a different bath is used each time. The oil which is stripped from the fibre forms an emulsion and imparts a white colour to the baths, hence the name *white baths*. The old white baths may be used for the preparation of fresh green liquors.

*9th Operation—Steeping.*—The yarn is steeped for further purification in water at 55° for 24 hours, washed well and stoved at 60°. If it still contains much unmodified oil a solution of sodium carbonate at  $\frac{1}{2}$ ° Tw. is used, the yarn steeped two hours in tepid water, washed and dried.

*10th Operation—Sumaching or Gallig.*—An infusion is prepared of 12 kgs. (12 lbs.) of best leaf sumach for every 100 kgs. (100 lbs.) of yarn, and the cold solution is filtered and diluted to  $1\frac{1}{2}$ ° Tw. The yarn, while still warm from the stoving operation, is steeped for six hours in the solution at 50° and then hydro-extracted. It thus takes up a certain amount of tannic acid.

*11th Operation—Aluming or Mordanting.*—Cake alum is dissolved in warm water, and, when nearly cold, a cold solution of one-fourth its weight of soda crystals is added. 15 to 20 per cent. of red liquor (16° Tw.) and 0.5 to 0.7 per cent. tin crystals (of the weight of the alum) are often added to the liquor, but these additions are not essential. The addition of stannous chloride is made to prevent ferric oxide from entering into the colour lake and to introduce tin in some form into the colour, to make the shade more fiery. In this solution, which is brought to a specific gravity of 8° Tw. and kept at a temperature of 40° to 50°, the yarn is steeped for twenty-four hours, then thoroughly washed and hydro-extracted. By this operation aluminium salts are formed with the previously fixed oxyfatty acids and tannic acid.

The yarn, which is at last ready for dyeing, should now possess a deep yellowish tinge.

*12th Operation—Dyeing.*—The goods are best dyed in wooden vats with closed stear coils of tinned copper. Iron vessels must be covered from time to time with a coating of insoluble iron tannate, by boiling out with a weak decoction of sumach; if this is not done the red shade will be rendered dull by iron compounds.

The water used for dyeing should indicate 2° to 3° of hardness (Clarke's

sate); if it contains little or no lime, a suitable amount of ground and washed chalk (about  $\frac{1}{2}$  per cent. of the weight of the 20 per cent. Alizarin paste employed) must be added. Very hard water, or water which contains iron, cannot be used in Turkey-red dyeing.

The dye-bath is prepared with madder or with 8 to 10 per cent. of Alizarin (20 per cent.), 1 per cent. of tannic acid (or 3 to 5 per cent. of good sumach), and about 30 per cent. of ox-blood (of the weight of the cotton). The yarn is entered into the cold dye-bath, the temperature gradually raised to boiling during one hour, and maintained so for 30 to 60 minutes longer. After dyeing, rinsing in water is advisable.

The goods now possess a dull red colour, which is transformed by the "clearing" processes into the brilliant Turkey-red shade.

*13th Operation—First Clearing.*—The yarn is boiled for four hours in open pans or under a pressure of 3 to 4 lbs. with about 3 per cent. of soda crystals and 3 per cent. of palm-oil soap, dissolved in a sufficient quantity of water. The clearing boiler of D. Stewart & Co., Glasgow, is shown in section and plan by Figs. 60 and 61. The boiler is made of copper, and the fittings either of copper or brass. The drawings show the false bottom (A), on which is fitted the (vertical) puffer-pipe (P) with the distributing cap (B) on top; under the false bottom a section of the steam-coil is visible, and on the floor level the draw-off pipe (D); on top of the boiler is fitted a blow-off with safety-valve (O). The principle of working resembles that of a bleaching kier. Arrangements are fitted to keep the liquor constantly passing through the goods, which rest on a perforated false bottom, shown in plan. The liquor is boiled by a steam-coil, and forced by the steam to the top of the puffer-pipe, so as to be spread over the goods by the distributing cap; this action is of an intermittent character, since after each boiling-over the steam under the false bottom must accumulate, until it is again able to overcome the weight of the column of water. The liquor, which is ejected through the puffer-pipe, circulates through the goods, and collects again under the false bottom.

*14th Operation—Second Clearing.*—The yarn is boiled for one to two hours at 3 to 4 lbs. pressure, with a solution of  $2\frac{1}{2}$  per cent. of palm-oil soap and 0.15 per cent. of tin crystals (of the weight of the cotton), and afterwards thoroughly washed in water. The excess of water is removed by mechanical means (hydraulic press or hydro-extractor), and then the goods are dried in an open-air shed. This closes the long chain of operations.

**II. Steiner's Process for Turkey-Red on Cotton Piece Goods.**—In Steiner's (of Accrington) process, the repeated green liquor baths and following laborious exposures of the hanks in the open air are replaced by one padding operation in hot clear olive oil, and subsequent treatment in various soda baths and stoving. The economy in time thus effected is considerable, and the colour becomes very fast and beautiful; indeed, of a greater brilliancy and intensity than can be obtained by the emulsion processes. The process is not used for the dyeing of yarns, on account of the difficulty of handling the yarn properly in the hot oil.

*1st Operation—Bleaching.*—The goods are well washed and boiled for two to three hours with water only, then boiled for ten to twelve hours in a solution of caustic soda, containing 2 kgs. (lbs.) of caustic soda for 100 kgs. (or lbs.) cotton, and washed; finally, boiled a second time for ten hours with caustic soda, 1.5 kgs. (or lbs.) for 100 kgs. (or lbs.) of cloth, and washed. They are then steeped for two hours in a solution of sulphuric acid ( $2^{\circ}$  Tw.) (*souring*), washed, padded in a weak solution of sodium carbonate ( $4^{\circ}$  Tw.)—to remove the least traces of free acid—and dried.

*2nd Operation—Oiling.*—The pieces are padded in open width in a clear solution of olive oil at a constant temperature of  $110^{\circ}$  C., and dried in the

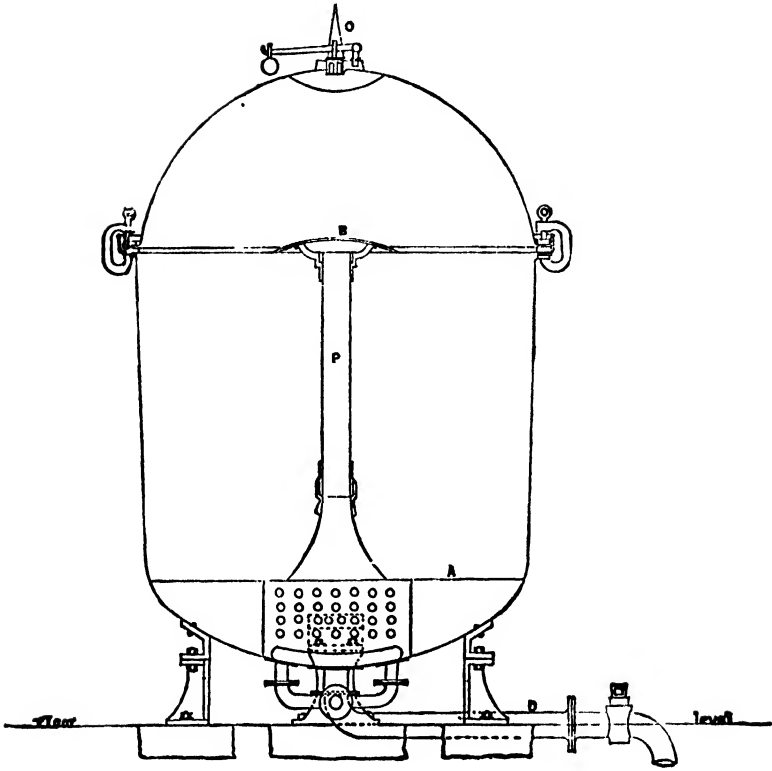


Fig. 60.

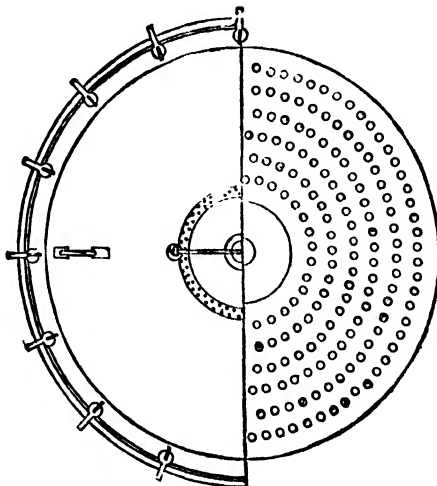


Fig. 61.

drying chamber, the temperature of which is brought as rapidly as possible up to 70°, and kept so for two hours. In this process no emulsive oil is employed. The oiling is done with specially-constructed machines. Fig. 62 shows an oil-padding machine of D. Stewart & Co., Glasgow. The machine consists

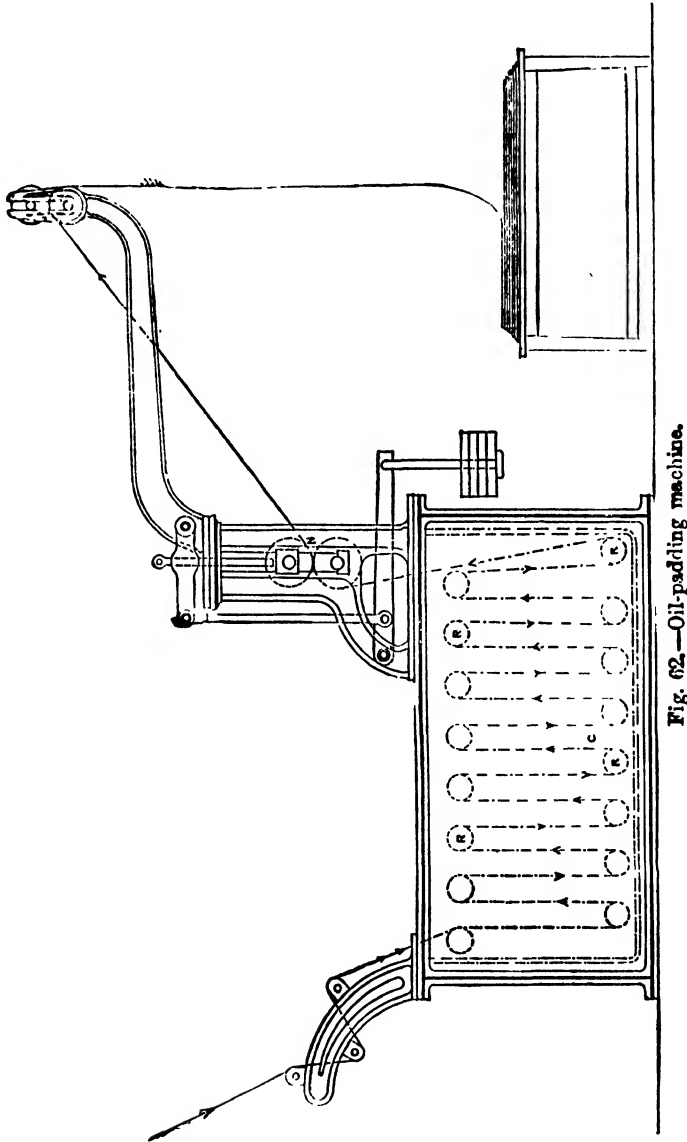


Fig. 62.—Oil-padding machine.

of a steam-jacketted cistern (C) for containing the oil, and maintaining it at a certain consistency and temperature. The outside is formed of cast-iron plates, and the inside of copper plates fixed at a distance from the cast iron, thus allowing a space for steam. Mounted inside the cistern are copper rollers (R), which guide the fabric during the immersion in the oil, after

which they pass between a pair of heavy nipping rollers (N), and are loosely folded down. The cloth is passed through the oil, as indicated in the figure; before it enters the cistern, it is well opened out, and made free from creases by three stretching-bars or "openers."

*3rd to 9th Operations—Liquoring.*—The oil which has been absorbed by the fibre during the hot oiling is fixed in the next operations by saponification; for this purpose, the material is impregnated with soda and hung up in heated rooms; a similar product of oxidation and polymerisation probably results thereby as in the old emulsion process.

These "liquoring" operations are totally different from those taking place in the "white baths" of the emulsion process, the latter being chiefly used for purifying purposes.

Fig. 63 shows a liquor-padding machine of D. Stewart & Co., Glasgow,

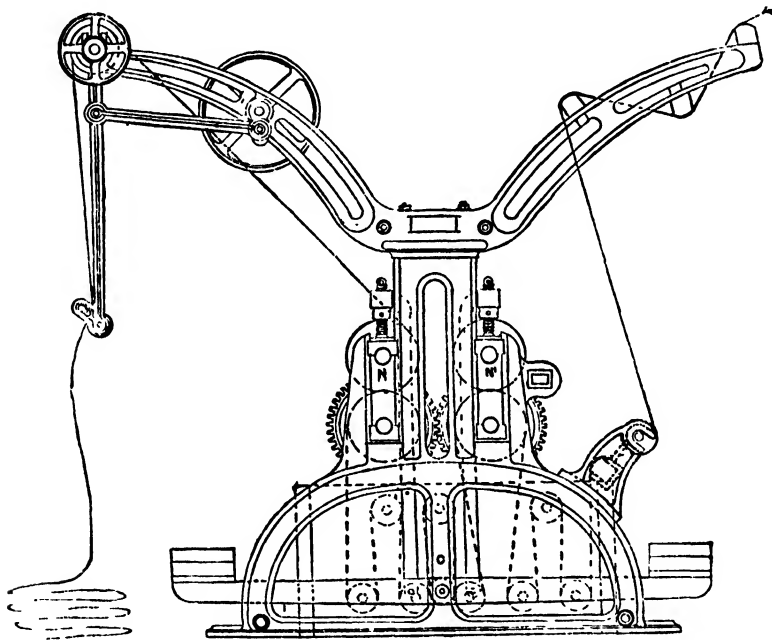


Fig. 63.—Liquor-padding machine.

which is constructed for the "liquoring" operations, and can be used for similar purposes. The liquor through which the goods are to pass is contained in a cistern (C) mounted with a number of rollers which guide the fabric during the immersion. Over this cistern two pairs of heavy nipping rollers (N, N<sup>1</sup>) are carried by suitable cheeks, and pressure is applied by a system of levers and weights. The nipping rollers are made of various materials, such as cast iron, brass, or block tin, according to requirements. The cloth enters on the right side of the drawing, is well opened out, passed over part of the rollers, squeezed by the nipping rollers, passed over the other rollers, squeezed again by the second pair of nipping rollers, and folded down.

The pieces are padded seven times in the open width in a solution of sodium carbonate (4° Tw.), and hung, after each padding operation, for two hours in a stove at 75° to 77°. In winter time the padding liquors are heated to 35° or 40°; in summer time the ordinary temperature is sufficient; if the

liquors become too hot, too much oil is stripped from the fibre. The padding liquors become in course of time veritable oil emulsions, and their specific gravity must be maintained regularly with great care in order to obtain an even and satisfactory shade.

The quantity of oil which is permanently fixed in the fibre depends on the number of "liquoring" operations; hence their number varies with the depth of the ultimate shade which it is desired to produce. Good Turkey-red which has been prepared by Steiner's process contains about 10 per cent. of modified oil in the fibre.

The drying rooms must be very well ventilated in order that the moisture which is given off may rapidly escape; otherwise the fibre is liable to be weakened.

**10th Operation—Steeping.**—The object of this operation is the same as that of the steeping in the emulsion process—viz., to free the fibre from all adhering oil which has not been fixed thoroughly. For this purpose the pieces are run through a vat which is divided into several compartments, fitted with rollers above and below. The first compartments are filled with sodium carbonate ( $\frac{1}{2}$  Tw.) at 40°, the last with water only; after being well washed the pieces are dried.

**11th to 14th Operations—Mordanting, Dyeing, and Clearing.**—These operations are exactly the same as those in the emulsion process.

The chemical reactions in Steiner's process cannot be explained more exactly than those in the old emulsion process. They are very similar and differ chiefly in the methods used for oiling the goods and for fixing the absorbed oil. They probably result in the production of the same or very similar compounds.

**III. New Turkey-Red Process ("Sulphated Oil" or "Turkey-Red Oil" Process)** for best Turkey-Red.—This process more closely follows the emulsion process, and, therefore, yields faster red, especially faster to mangling than the following method.

In the following we give a process which has given great satisfaction in practice, and begins with the preparation of the necessary oil mordant.

Eighteen kgs. (40 lbs.) best castor oil are mixed gradually and without development of much heat with 2½ kgs. (5.5 lbs.) sulphuric acid in a pot holding 30 litres (6.6 galls.). The pot is placed, during the mixing, in a vessel filled with cold water and allowed so to remain until the oil gives a clear solution with potash and ammonia; this requires about two days in summer time, three or four days in winter time, and even more during very cold weather. The acid oil thus obtained is used without washing or neutralising.

For 300 kgs. (660 lbs.) of cotton yarn the working is as follows:—

(1) *Boiling*, as in the emulsion process, the steeping liquor with the addition of 7½ kgs. (16½ lbs.) soda being used. Rinse and oil without drying.

(2) *First Oiling (Green Liquor)*.—The bath is used continuously and freshened up with 22 kgs. (48½ lbs.) acid oil, 5 kgs. (11 lbs.) ammonia, and 22 litres (4 galls. 7½ pints) solution of potassium carbonate 1.26 specific gravity (52° Tw.). For a fresh bath 2½ times these quantities (50 kgs. acid oil, &c.) are necessary. The yarn is oiled in this liquor at 40° to 45°, as in the emulsion process, and then dried in stoves heated to 70° or 75°.

(3) *Second Oiling* like the first oiling.

(4) *Third Oiling*.—This is done in a standing bath with 20 kgs. (44 lbs.) acid oil and 44 litres (9 galls. 4½ pints) potash solution (or correspondingly more in a fresh liquor). Stove as before. This oil bath is much more alkaline than the two preceding baths, and, therefore, it has a stripping effect similar to the white liquor baths in the emulsion process, but at the same time it exerts an oiling action.

(5) *Steeping*.—The yarn is placed for eight hours in water of 30° to 35° C., then hydro-extracted and stoved at 70° to 75°. The liquor draining from the yarn amounts to 900 litres (200 galls.) of 1.01 specific gravity (2° Tw.), and is used to dilute the oil baths (green liquors) and for boiling-off the grey yarns.

(6) *Aluming or Mordanting*.—This bath is also used continuously, and freshened up with 50 kgs. (110 lbs.) aluminium sulphate, 4.25 kgs. (9½ lbs.) soda crystals (in solution), and the same quantity of chalk, and also 1 kg. (2.2 lbs.) tannic acid; the whole is well mixed, and the clear solution, drawn off the settled precipitate, is diluted to 1.03 specific gravity (6° Tw.) and used for mordanting. The dry yarn is evenly put into a wooden vat, and during the depositing the mordanting liquor is poured over the yarn and then, without working, allowed to act for fifteen to twenty hours. The liquor is then drawn off for further use and the yarn well rinsed, but, in order to avoid unevenness, not hydro-extracted. The yarn is not dried.

(7) *Dyeing*.—The dye-bath is prepared for 100 lbs. of yarn with about 6½ kgs. (14½ lbs.) Alizarin and 100 grms. (3½ ozs.) tannic acid, and in the case of water which is not very calcareous with ¼ to ½ kg. (½ to 1 lb.) ground chalk. The mordanted, wet yarn is turned one hour cold, the bath is then heated to boiling in the course of one and a half hours when the yarn is put under the surface of the liquor and the boiling continued for one hour.

(8) *First Clearing*.—Three hours' boiling at 20 lbs. (1½ atm.) pressure with the addition of 3 to 4 kgs. (6½ to 9 lbs.) soda, followed by rinsing.

(9) *Second Clearing*.—Four hours' boiling at 20 lbs. (1½ atm.) pressure with 8 kgs. (17½ lbs.) neutral soap, ½ kg. (1.1 lbs.) soda, and 400 grms. (14 ozs.) tin crystals, followed by rinsing and drying in the air.

IV. *New Turkey-Red Process ("Sulphated Oil" or "Turkey-Red Oil" Process) for Yarn and Piece Goods*.—This process also yields beautiful red shades, which are, however, not quite as fast as those obtained by the preceding process.

The process resembles that given in the beginning of this chapter (p. 565) for the mordant colours generally, and may replace it.

Turkey-red oil prepared from castor oil is most generally used; sulphated olive oil can be employed, but has not proved so good, as it does not oxidise and polymerise as readily. Very good results are obtained with a carefully made castor-oil soap—i.e., sodium ricinoleate, but this is not used on the large scale.

*1st Operation—Boiling*.—This is done exactly in the same way as in the preceding processes. Bleaching has to be resorted to in the case of light shades (especially pinks) to obtain bright tints, but the action of the chlorine has to be restricted as far as possible to the destruction of the natural colouring matters of the cotton fibre, while the formation of oxycellulose must be prevented; for this reason, hypochlorite of soda is preferable to bleaching powder, or better still is bleaching with potassium permanganate.

*2nd Operation—Oil-preparing*.—The washed goods are hydro-extracted, but not dried, and then worked in a bath containing 10 to 20 kgs. (lbs.) of neutralised Turkey-red oil (50 per cent.) for every 100 litres (10 galls.) of water. When thoroughly saturated with the liquor they are evenly wrung out.

*3rd Operation—Stoving*.—The oiled goods are dried at temperatures ranging from 40° to 60°. For the production of a bright and intense red the operations of oiling and drying and subsequent aluming are repeated once or twice. Frequently the oiled goods are steamed under a pressure of 8 lbs. for sixty to ninety minutes, but this is not essential.

The compounds constituting the Turkey-red oil are decomposed by the operations of oiling, drying, and steaming, ammonium or sodium sulphate and



various organic acids being formed. The latter are similar to the corresponding substances deposited in the fibre in the older processes, and consist of products of the oxidation and polymerisation of ricinoleic acid, &c.

*4th Operation—Aluming.*—The goods are worked for five or six hours in a warm bath (40° to 45°) of red liquor (10° Tw.), or of basic aluminium sulphate (10° Tw.), well wrung out and dried at 40° to 50°.

*5th Operation—Chalking.*—This resembles the treatments in the other Turkey-red processes by which the material is worked in a weak alkaline bath for the purpose of purifying it from an excess of oil; in this process, however, the purification takes place after the aluming, so that not only is there a removal of oil, but also a more complete precipitation of the alumina which has been absorbed by the fibre during the aluming. A chalk bath is generally employed for this purpose (*chalking*). Brighter colours are said to be produced when phosphate of soda or ammonium carbonate are employed as fixing agents.\* Arsenate of soda gives still brighter colours than the phosphate. The cotton is worked for thirty minutes at 30° to 40° in a bath containing  $\frac{1}{2}$  kg. (lb.) of ground chalk per 100 litres (10 galls.) of water, then thoroughly washed and dyed without drying.

*6th Operation—Dyeing.*—Moderately hard water, free from iron, exactly as in the emulsion process, is required. For very deep shades about 15 per cent. of Alizarin (yellow shade) is necessary; a fine pink is obtained by this process with 1 to 2 per cent. of Alizarin V (purest quality of Alizarin blue shade). The whole quantity of the dyestuff is added to the dye-bath, and the goods are introduced at a temperature not exceeding 25° and turned for twenty minutes; in about half an hour the bath is heated to 60° or 70° and maintained at this temperature for one hour (see also p. 593). After dyeing, the goods are wrung and dried with or without previous washing.

*7th Operation—Second Oil-preparing.*—The material is impregnated once more with a solution of neutralised Turkey-red oil (5 to 10 kgs. or lbs. per 100 litres or 10 galls.) and dried. The second oiling may be dispensed with or take place after the mordanting. In the latter case a fresh treatment in a weak solution of basic aluminium sulphate or red liquor follows for the purpose of fixing the oil.

*8th Operation—Steaming.*—The goods are steamed for one hour at 15 lbs. pressure or two hours without pressure to develop the colour. According to a more recent process, neither oiling nor steaming follows the dyeing; the dyed goods are simply heated for some hours in water under considerable pressure. It is said that the beauty increases up to a pressure of about 65 lbs. When the goods come from the dye-bath they possess an orange tinge and a part of the dyestuff can be stripped by rinsing in water, since it is not intimately combined with the mordants. The complex lake is formed by steaming only, and the material then receives a dull red colour which is brightened by the clearing baths. Fig. 64 shows a steaming box which may be used both for yarns and for piece goods. It consists of a horizontal cylinder, one end of which is closed by a sliding door balanced by counterweights. A part of the shell is left out in the drawing so as to show the inside arrangements. The hanks or pieces are suspended on a movable framework on rails provided with bevelled wheels, which can be turned from the outside; turning is of advantage in order to ensure regularity in the steaming and to prevent rail marks; this arrangement, however, is not found in all steaming boxes.

*9th and 10th Operations—First and Second Clearings.*—These operations may be executed as in the older processes; but less severe treatments are sufficient. A fine brilliant red is produced by once or twice boiling under

\* J. Wolf, *Journ. Soc. Dyers and Col.*, 1885, p. 207; Kutschera and Utz, *Journ. Soc. Chem. Ind.*, 1886, p. 531.

4 to 8 lbs. pressure for thirty to sixty minutes in  $\frac{1}{2}$  per cent. soap solutions (without any further additions). The soaped goods are well washed in water and dried at a moderate temperature.

The process can be simplified by raising the temperature of the dye-bath to the boiling point. In this case the oiling after dyeing is to be omitted, and the steaming may be dispensed with. But the shade is never so bright or fast

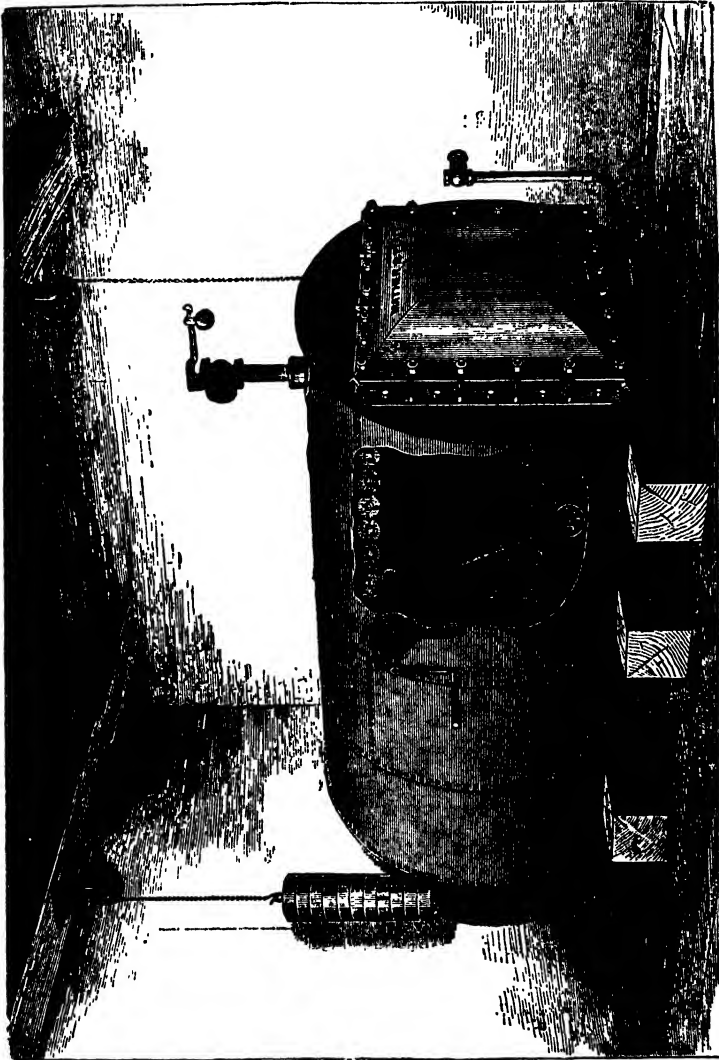


Fig. 64.—Steaming cottages.

as that of the colours which have been produced at a lower temperature with subsequent steaming.

The simpler process, however, is well adapted for the other Alizarin colours, since these require no steaming, and a light soaping only. They are dyed with advantage in this manner (see p. 563).

**ALIZARIN RED DYEING PROCESSES.**

By the following methods aluminium-calcium Alizarin lakes are also formed, and fatty acids are introduced into the lakes in some way. But the methods of dyeing and the resulting colours are essentially different from those of Turkey-red processes:—(1) Inasmuch as the oil is not fixed on the fibre before the mordanting and dyeing, and (2) for the fact that the ultimate colours are inferior in brilliancy and in fastness to air and light, to soap and chlorine. The inferiority of the Alizarin reds is undoubtedly due to the quantities of oil that are applied being much smaller, and to the time for their transformation being shorter than in the Turkey-red processes. But it cannot be said whether the ultimate cause is a different chemical composition of the colour lake, or the absence of the supposed oil-varnish around the colour.

**I. Alizarin Red or New Red Process, with Aluminium Acetate.**—The process resembles the old “madder dyeing”; but it is much simpler, since the artificial dyestuff is much easier to dye with than the natural product. The goods are bowked, and then directly mordanted in commercial red liquor (aluminium acetate) 5° to 8° Tw. The goods may also be padded once or twice on the padding or printing machine; but in this case stronger liquor with some thickening is required—*e.g.*, 5 litres (5 galls.) of red liquor (22° Tw.), 3 litres (3 galls.) of gum tragacanth thickening (75 grms. of gum per litre, or 12 ozs. per gall.), and 6 litres (6 galls.) of water.

The material, mordanted either way, is aged for seventy-two hours in an ageing room in which the temperature is 35° C. by the dry-, and 30° by the wet-bulb thermometer; acetic acid is driven off by the ageing, and aluminium hydroxide (or a very basic aluminium acetate) is precipitated in the fibre. In order to fix the mordant better, the goods are worked for five minutes at 60° in a bath made up with a solution of phosphate, arsenate, or silicate of soda, to which, as a rule, some cow-dung is added. The bath may also be prepared with 5 litres ( $\frac{1}{2}$  gall.) of silicate of soda (75° Tw.), 1 kg. (1 lb.) of chalk, 10 litres (1 gall.) of cow-dung, and 1,000 litres (100 galls.) of water. For piece goods a vat is used, which is fitted with rollers above and below. When coming from this bath the material is washed well in water, and is then ready for dyeing. Piece goods are dyed in rope-form, run over a winch. 8 to 15 per cent. of Alizarin, yellow shade, and half as much neutralised Turkey-red oil, are added to the bath. (The usefulness of the oil in the dye-bath is disputed, and it is claimed by some that it causes a loss of Alizarin.) One-half per cent. of tannic acid of the weight of the Alizarin is added with advantage to the dye-bath. As to the quality of the water, and the addition of chalk or calcium acetate, we refer to the remarks on Turkey-red dyeing. The dyeing is started cold, and the temperature raised during two hours to 60° or 70°, but not higher. After dyeing, the cotton is washed, dried, and impregnated with a solution of 1 litre (1 gall.) of Turkey-red oil in 10 litres (10 galls.) of water, and dried in the drying-room. Finally, the goods are steamed for one hour under 20 lbs. pressure, or for a longer time at a lower pressure, soaped in  $\frac{1}{2}$  per cent. soap solution at 75° for one hour, rinsed in water, and dried in the drying-room. Some dyers, however, soap a second time at the boil. Alizarin G must not be soaped at the boil.

This process still offers difficulties for piece dyeing, and is hardly used on yarns. Great care is necessary to obtain level colours when pieces are dyed in rope form, and dyeing in the jigger is also not entirely satisfactory. According to Th. Baldensperger, the dyeing proceeds easily and rapidly when the Alizarin is dissolved in ammonia. The goods may be entered lukewarm, and the bath rapidly heated to the boil, or dyeing may begin at the boil. One hour is sufficient for dyeing three pieces in the jigger, whereas dyeing on

the winch would require three hours. The process also allows economies in dyestuff, steam, and labour. Enter the mordanted goods into water prepared with a calcium salt, fill up with water, heat to 50°, and add the dissolved Alizarin in two or four portions, depending on the length of the pieces. Run half an hour without boiling, and a quarter of an hour boiling; after ten passages the tissue is well dyed and the bath nearly exhausted; the tissue is now washed and brightened as usual. The colour solution is prepared by dissolving 10 kgs. (lbs.) Alizarin in 40 litres (4 galls) water containing 1 kg. (lb.) ammonia. Dyeing in limewater alone gave only moderate results. (See also the following processes, especially those of Schlieper and Baum, and of Erban and Specht, in which also solutions of Alizarin in limewater or ammonia are used.)

II. Schlieper's Alizarin Red Process, with Aluminate of Soda (*continuous process for Alizarin Red on Piece Goods*).—The goods are bowked as usual, and then impregnated with a solution of aluminate of soda prepared in the following manner:—*Alkaline alumina mordant*: 100 kgs. (100 lbs.) of gelatinous alumina (commercial) are dissolved in 160 litres (16 galls.) of caustic soda (62° Tw.), and diluted with water to make 750 litres (75 galls.); 20 litres (2 galls.) of hydrochloric acid (31° Tw.) are added; the whole is then made up to 1,550 litres (155 galls.), and allowed to settle. For padding, this solution is diluted with  $\frac{1}{4}$  of its volume of water. Some dyers add to it besides a small quantity of sodium stannite (solution of stannous oxide in caustic soda). After padding, the pieces are dried on cylinders, when they assume a yellow colour; they are then aged for twelve to twenty-four hours in ageing rooms until the original colour is restored. The goods are then passed through a vat, with rollers above and below; first through cold water, or through a solution of ammonium chloride or silicate of soda, and then through a tepid chalk bath. A thorough washing follows. The dyeing takes place on a jigger, through which the pieces pass slowly in open width during three to four minutes at 90° to 95°. The bath contains per litre (per 100 galls)  $\frac{3}{4}$  gm. (12 ozs.) of Alizarin, and 6 grms. (6 lbs.) of clear lime-water. (As stated on p. 573, acid and basic calcium alizarate are soluble in water.) After this follows a padding in Turkey-red oil (5 to 10 parts in 100), or, better, in a specially-prepared soap emulsion; then a steaming for one hour under 15 lbs. pressure; and, finally, soaping as usual, washing, and drying.

The soap is prepared by saponification of castor oil with caustic soda-lye, and subsequent addition of sufficient hydrochloric acid to neutralise one-half of the soda; an emulsion of this acid soap in water is used.

III. Alizarin Red, Erban and Specht's Method.—Erban and Specht's process\* differs totally from all previously described Alizarin red and Turkey-red processes by the fact that the mordanting follows the dyeing.

The fibre is first impregnated with a solution of Alizarin in an alkali, and afterwards with the corresponding mordant; by steaming, the colour lake is developed. Alizarin is dissolved in ammonia, and in the more or less diluted solution the tissue is padded (for dark shades twice) and then dried; the ammonia evaporates, and the colouring matter remains in an undissolved state in the fibre. Besides the alkaline solution of Alizarin, the bath may receive additions that will not precipitate the colouring matter—for instance, aluminate of soda, soap, stannate of soda, or Turkey-red oil; for light shades a second bath (mordanting bath) may be thus avoided. The dried tissue is brought into the second bath (which contains the metallic mordants, the best being those which are salts of a volatile acid, as, for example, the acetates), and is dried again. By this process the formation of the colour lake is initiated. Steaming for one to two hours under 20 to 30 lbs. pressure, and clearing

\* German Patent 54,047, *Journ. Soc. Dyers and Col.*, 1890, p. 182.

follow ; before steaming, it is advisable to oil the goods with Turkey-red oil or soap. The same method is recommended for the dyeing and printing of Alizarin and similar dyestuffs with various mordants, such as the acetates of aluminium, calcium, chromium, and iron.

The Hoechst Farbwerke have patented \* a single-bath process by which the previously oiled cotton is dyed in a mixture prepared by grinding together Alizarin, aluminium sulphate (or a chromium or iron salt), and sodium bisulphite. This process, however, does not appear to have acquired any practical importance.

**IV. Alizarin Red on Cops.**—The dyeing of Alizarin red on cops in dyeing machines still seems to be in an experimental stage. From time to time it has been announced that this problem has been solved, but Alizarin-dyed cops are not yet a regular commercial article. Some years ago it was claimed that the difficulty caused by the insolubility of the Alizarin lime compound had been overcome by the use of calcium saccharate † in the following way:—For 35 kilos. cotton yarn, 4,300 grms. Alizarin 20 per cent., 230 grms. soda ash, 860 grms. calcium saccharate, and 80 grms. tannic acid if desired are dissolved in 1,000 to 1,200 litres water. The yarn is treated in this bath, and then steamed at 1 to 1½ atmospheres pressure for one to two hours. This process is in use in the dyeworks of Feitis and Kornfeld, of Prague. L. v. Süsskind has recommended to substitute strontium bisaccharate for the calcium salt. ‡ It may be mentioned in connection with this question that, according to F. Erban's German Patent 200,682, Alizarin preparations soluble in calcareous water are obtained by heating Alizarin with gelatin or glue together with borax. According to a recent patent of the Schlesische Türkischrot-Färberei, § the cotton is prepared in the usual way, but instead of the dye-bath being made up with Alizarin, alkali, and hard water, soft water (rain or condensed water) is used, and an addition of clear limewater is made. A small quantity of tannin is also added to the bath. The improvement is very marked in the dyeing of yarn on bobbins, &c. The dyeing is started in the cold, and the temperature is raised slowly. On leaving the dye-bath the cotton is treated with dilute acid, to which a little stannous chloride has been added. It is finally steamed and brightened. A similar process of dyeing Alizarin red in alkaline solution on cops has also been patented by the Rheinische Cops-Färberei Gesellschaft in Germany (German Patent 86,142). The cotton, mordanted as usual, is dyed in a solution of Alizarin in sodium carbonate, treated in acetic acid, and steamed.

**Alizarin Pinks.**—Pink shades are dyed with Alizarin on cotton by the methods already described ; the Turkey-red oil and the various Alizarin red processes are employed, but a smaller amount of colour lake is produced in the fibre. The aluminium mordant, therefore, is applied in a more diluted form, and basic salts are avoided because they give rise to uneven dyeing, owing to the fibre taking them up too rapidly. Neutral aluminium acetate, and even normal aluminium sulphate at about 10° Tw., are used, while the quantity of oil for preparing before or after dyeing is correspondingly diminished. The dyeing is effected with 1 to 2 per cent. of purest Alizarin, blue shade.

Owing to the difficulty of obtaining a perfectly level pink with Alizarin on cotton piece goods, it is a common practice to pad the pieces with an Alizarin pink printing colour, dry, and develop by steaming.

\* English Patent 4115, 1900 ; *Journ. Soc. Dyers and Col.*, 1901, p. 124.

† F. Kornfeld, English Patent 15,639, 1900 ; *Journ. Soc. Dyers and Col.*, 1901, p. 219 ; *Färberzeitung*, 1909, p. 50.

‡ French Patent 352,328 ; *Journ. Soc. Dyers and Col.*, 1906, p. 74.

§ English Patent to A. Koblichke, 26,414, 1907 ; *Journ. Soc. Dyers and Col.*, 1909, p. 88.

**Alizarin on Chromium Mordants.**—Claret-red and maroon shades are produced with Alizarin on chromium mordants, which are very fast to light, soap, and chlorine, but not equal in this respect to the aluminium and iron shades.

The general methods for mordanting and dyeing are indicated in the introduction to this chapter (p. 566). In using chromium mordant G A I (M.L.B.) for dyeing with Alizarin, the commercial article should be diluted with twice its volume of water only. Redder shades than those produced with chromium mordants alone can be obtained by a combination of chromium and aluminium.

The dye-bath is prepared with the dyestuff—for deep shades about 8 per cent. Alizarin—and with some calcium acetate—about one-fourth to one-fifth of the weight of the Alizarin paste. If very hard water (30° or more on Clark's scale) be used the addition of the calcium salt may be dispensed with. The goods are introduced into the cold dye-bath, which is heated in the space of one hour to boiling and maintained at this temperature for two hours longer. They are then well rinsed in water, and finally soaped at 60° or at the boil, washed and dried.

Alizarin, blue shade, and Alizarin, yellow shade, can be dyed on chromium mordants; the former gives bluer and more brilliant tints.

**Alizarin on Iron Mordants.**—Alizarin dyeing in association with iron mordants has been practised for many years. Violet shades equalling in fastness the best Turkey-reds are obtained by the Turkey-red methods by substituting a ferrous salt for the aluminium compounds and fixing it as a ferric compound in the fibre. Good lilac, purple, and dark violet shades are produced in this way. They can be obtained, however, of very satisfactory quality by less expensive methods, as there is a less demand for extremely fast colours in these tints than for fast Turkey-reds. Hence the material is not oiled (or but slightly oiled) before mordanting, and the process is chiefly used for the dyeing of cotton piece goods or for calico-printing. Alizarin, blue shade, is required, since Alizarin, yellow shade, does not give pure tints with iron mordants.

Ferric salts are not suitable for mordanting, as they give rise to rubbing if precipitated as such; permanent colours are not obtained unless the ferrous compounds are oxidised after they have been taken up by the fibre. The best iron mordant is ferrous acetate or pyrolignite of iron; it gives brighter and bluer shades than ferrous sulphate, and is more readily fixed. The latter is not a good mordant, especially on unprepared cotton, since, after ageing, the fibre retains only a small amount of the oxide. It can be fixed, however, much better by means of a double salt of copper arsenite and calcium arsenite, prepared by boiling 1 kg. (1 lb.) of white arsenic and 1 kg. (1 lb.) of copper sulphate in 90 litres (9 galls.) of limewater, and allowing to settle, the clear solution being added to the fixing bath or print colour (*Schuetzenberger*). Oscar Scheurer\* has shown that the arsenic can be replaced by phosphoric acid, 2 parts of the latter being mixed with 3 parts of copper sulphate (see p. 267).

The amount of iron which is taken up by the fibre depends less on the strength of the mordanting liquor than on the amount of oil that has been already fixed in the material; the oil attracts the oxide of iron with great energy, so that it is not readily stripped from the fibre, even by comparatively concentrated sulphuric or hydrochloric acid. The best and bluest shades are obtained if the iron-mordant is thoroughly saturated with Alizarin, while an excess of mordant imparts an unpleasant dull-red appearance; hence only a moderate preparation with oil is required for light shades, whereas for dark violets a strong oiling is of advantage.

\* *Journ. Soc. Dyers and Col.*, 1887, p. 193.

Very deep purplish-blacks are obtained with little or no oiling by mordanting the cotton with tannin and iron by one of the methods given in Part V., pp. 188-190, and 266-268. A good dark purplish-violet is produced by impregnating the cotton with iron pyrolignite (12° Tw.), drying, ageing in the Mather and Platt apparatus, and then for two days in ageing rooms, dunging in cow-dung and arsenate or silicate of soda, washing, and dyeing.

By whatever method the material has been impregnated with an iron salt, it is always passed through some fixing bath before the dyeing begins. A chalk bath is sufficient for thoroughly oiled cotton; a "dunging" bath, however, is required if the iron is only partially or not at all fixed with the aid of oil. The dunging bath, which is prepared with cow-dung and arsenate, phosphate, or silicate of soda, is used both to fix the iron completely in an insoluble form, and to remove all that has not been well fixed in the fibre. After a thorough washing, the material is ready for dyeing.

It has been previously shown that a ferric-ferrous Alizarin lake can be obtained analogous with the violet ferric-calcium alizarate and the red aluminium-calcium alizarate. This ferric-ferrous compound is probably formed if sodium arsenite is added to the dye-bath, as is frequently done in order to produce faster and brighter shades. Notwithstanding this, in dyeing with very soft water some chalk or acetate of lime ( $\frac{1}{2}$  per cent. of the weight of the 20 per cent. Alizarin paste) should be added to the dye-bath.

The dye-bath is made up with the required amount of dyestuff—8 per cent. of Alizarin V for a full shade—and about 5 per cent. (of the weight of the material) of neutralised Turkey-red oil. For bright violets 5 to 10 per cent. of Methyl-violet (of the weight of the Alizarin paste) is also added to the liquor. The cotton is introduced into the cold dye-bath, and the temperature is raised during one and a-half hours to 75°. After dyeing, the cotton is washed, dried, steamed under 15 lbs. pressure for twenty minutes, and soaped at 60°.

Various shades of claret-red, puce, and chocolate are obtained by mordanting the cotton with a mixture of aluminium and iron salts. Some difficulty is met with in fixing the necessary quantity of iron; to overcome this, it is recommended to impregnate the cotton with tannin before mordanting with a mixture of the aluminium and iron salts; sometimes it is effected by adding arsenic or arsenite of calcium and copper to the fixing (dunging) bath. The arsenic may be replaced by phosphoric acid. Oscar Scheurer (*l.c.*) has drawn attention to the fact that in red liquor some sulphuric acid is generally present, forming ferrous sulphate, which compound is, as stated above, not readily fixed. The combined mordant is aged and dunged like the iron mordant alone, and the dyeing proceeds as with the iron mordant.

Moderately fast orange shades can be obtained with Alizarin on cotton mordanted with *stannic oxide*; these, however, are not produced as self-colours; but use is made of this fact in Turkey-red dyeing to give the shade greater fire, as has been repeatedly noticed.

**Dyeing of Alizarin on Linen.**—Linen may be dyed with Alizarin by processes similar to those used for cotton. The effect, however, is less satisfactory owing to the linen fibre being less permeable than cotton.

Jute is not dyed with Alizarin (as stated above), since the dyestuff and the process of dyeing are too expensive for this material.

**Dyeing of Alizarin on Wool.**—The use of madder has not been restricted to cotton and linen dyeing; it has been applied from an early period to the production of fast wool colours, particularly for the dyeing of fast reds on military cloth. The French Government under Louis Philippe introduced the

red trousers for the French army with a view to encouraging the madder culture. Even at the present time madder is still used in small portions in wool dyeing, because it is easier to obtain level shades with madder than with Alizarin. But it has now been replaced very generally by Alizarin. The methods of Alizarin dyeing having been very much improved, there exists no necessity of using madder, which has the great disadvantage of leaving much dust in the wool.

Observations on the general methods of dyeing wool with Alizarin, and especially the precautions required for the production of thoroughly satisfactory colours, are given at the beginning of this chapter (p. 567).

*Dyeing with Aluminium Mordants.*—Alizarin yields, on wool mordanted with aluminium salts, red shades which are very fast to light and most other agents, but become more bluish by milling and are always prone to rub. By the addition of tin crystals to the aluminium mordant more yellowish or scarlet shades are produced, which are still less fast to milling. The vessels employed both for mordanting and for dyeing should be made of tinned copper or wood. Care should be taken that there is no untinned copper in any of the baths employed, since this injuriously affects the colour.

(a) *Mordanting and Dyeing Method.*—The mordanting liquor is prepared with 6 to 10 per cent. of aluminium sulphate and 5 to 8 per cent. of tartar; the latter may be replaced, partly or completely, by oxalic acid or sulphuric acid (see p. 238); in a diluted bath the sulphuric acid acts but slowly, and its quantity has to be increased. Hard water is corrected with acetic acid. For more brilliant scarlets which are not to be milled severely, 1 per cent. of tin crystals is sometimes added to the mordanting bath; in this case, tartar or oxalic acid should be used, not sulphuric acid.

The well-purified and thoroughly-wetted wool is introduced into the mordanting bath at a low temperature, the liquor is heated for one hour to boiling, and maintained thus for thirty to sixty minutes. After being thoroughly washed in water, the wool is ready for dyeing.

About 10 per cent. of Alizarin (20 per cent.) is required for a full shade. The Badische Anilin- und Soda-Fabrik recommends an addition of one-fifth part of calcium acetate, one-tenth part of neutral soap, and one-twentieth part of tannic acid (of the amount of the Alizarin paste) to the dye-bath to obtain colours which are fast to milling; soap, however, should be used for goods only which are to be subjected to a strong milling, since it makes the colour disposed to rub. If sulphuric acid is employed in the mordanting bath, it is advisable to add 5 per cent. of sodium acetate (of the weight of the wool) to the dye liquor. The wool is introduced into the cold dye-bath, which is heated in forty-five minutes to boiling and kept so for one and a half hours.

(b) *Single-bath Method.*—For light shades the mordanting and dyeing operations can be combined at a considerable saving, although the dyestuff is not so completely utilised as by separate mordanting and dyeing. The bath is prepared with 3 per cent. of alum, 2 per cent. of oxalic acid, and the necessary amount of dyestuff. If the water is soft, some calcium acetate is added. The wool is entered at 20° to 30° and worked in the bath for twenty minutes; an hour is occupied in raising the temperature to the boiling point, at which it is maintained for one hour more. The shade is not so full, and does not possess the bloom of the red dyed by the two-bath method. It stands the action of light very well, but in milling it becomes lighter. The addition of a little stannous chloride to the bath renders the shade considerably brighter, but at the same time yellower.

*Dyeing with Chromium Mordants.*—By far the largest amount of Alizarin used in wool dyeing is applied in conjunction with chromium mordants. The shades are exceedingly fast to light and most other agents; they resist milling



very well, although they are somewhat changed and are more or less affected by mineral acids (carbonising). Fast claret to maroon shades are produced with Alizarin on chromium mordants; by the addition of aluminium sulphate to the mordanting bath more reddish shades are obtained. The general method is indicated in the beginning of this chapter (p. 568). Wool is usually mordanted with chromium by boiling it with 3 or 4 per cent. of bichromate of potash or soda with or without 1 per cent. of sulphuric acid. Sulphuric acid makes the shade more yellowish and fuller. The best results are obtained by mordanting with 3 to 4 per cent. of bichromate and  $2\frac{1}{2}$  to 3 per cent. of tartar. About 15 per cent. of Alizarin paste (of the weight of the wool) are required for a full shade.

The addition of calcium salts to the dye-bath is not absolutely necessary, but it makes the shade bluer and fuller; about 2 to 4 per cent. of calcium acetate (of the weight of the wool) are used.

Both the "mordanting and dyeing" and the "single-bath" methods are employed; the latter gives excellent results, and shades almost as full as those obtained by the two-bath method, and equally fast to light and milling. For a full shade in a single bath, 15 per cent. of Alizarin and 3 per cent. of bichromate of potash or soda are used. In order to obtain through and even shades, it is necessary to work first for some time in the cold, then to raise the temperature gradually to boiling, and to keep the liquid at the boil for some time.

*Dyeing with Iron Mordants.*—Alizarin yields on wool that has been mordanted with ferrous sulphate and tartar good violet to slate colours, which, however, are not quite fast to milling, and are also too expensive, on account of the considerable quantity of tartar necessary for mordanting. Good and full shades demand up to 30 per cent. of tartar. The mordanting is done in a bath with 4 to 12 per cent. of ferrous sulphate, and about double that amount of tartar; the dyeing takes place in a fresh bath with 10 per cent. of Alizarin and 5 per cent. of calcium acetate, using the same precautions as with the other mordants.

The single-bath method gives similar results.

*Dyeing with Tin Mordants.*—Alizarin produces with stannous chloride an orange shade on wool, which is very fast to light, but is affected by milling. The presence of calcium salts in the dye-bath is not essential; 4 to 5 per cent. of calcium acetate makes the shade orange-red, an excess of calcium salt still redder, but it causes uneven dyeing; in the absence of lime the shade is much more yellowish.

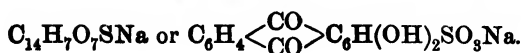
(1) *Mordanting and Dyeing Method.*—Mordant the wool with 4 per cent. of tin crystals and 2 per cent. of oxalic acid; dye with 10 per cent. of Alizarin with or without calcium acetate, as indicated for the other mordants.

(2) *Single-bath Method.*—The shade obtained with 10 per cent. of Alizarin, 4 per cent. of tin crystals, and 2 per cent. of oxalic acid in one bath is as good, if not better, than one obtained by mordanting and dyeing in separate baths. The bath is exhausted.

*Dyeing with Copper Mordant.*—Wool mordanted with copper sulphate yields a dull violet shade with Alizarin; it is of no practical value. A combination of chromium and copper mordant ( $1\frac{3}{4}$  per cent. of bichrome, 1 per cent. of copper sulphate with or without  $2\frac{1}{2}$  per cent. of tartar) is sometimes employed when Alizarin colours are dyed together with wood colours.

*Nickel-ammonium sulphate* and *uranium salts* yield useful shades of grey and slate with Alizarin, on wool.

*Dyeing of Alizarin on Silk.*—Silk is dyed with Alizarin in conjunction with aluminium, chromium, and iron mordants by the methods given on p. 570. About 20 per cent. of Alizarin is required for a full shade.

**ALIZARIN S, WS, or W (ALIZARIN, POWDER; ALIZARIN CARMINE).**

This is the sodium salt of Alizarin monosulphonic acid obtained by the action of fuming sulphuric acid on pure Alizarin.

Alizarin 2 S and Alizarin 3 S or 3 WS are very similar products, which are produced by treating Alizarin G with fuming sulphuric acid; they consist of sodium monosulphonates of Anthra- and Flavo-purpurin, and of small quantities of Alizarin S. Alizarin S is the most bluish and Alizarin 3 S the most yellowish brand, while Alizarin 2 S possesses an intermediate shade.

Alizarin S forms an orange powder, easily soluble in water with a yellow colour. Hydrochloric acid has no action on this solution, while caustic soda produces an intense reddish-violet colouration. The reaction is so delicate that this dye can serve as an indicator. Concentrated sulphuric acid dissolves the dyestuff with a brownish-yellow colour, which becomes yellow on diluting with water. Alum precipitates the dyestuff from the aqueous solution as orange flakes, which redissolve, on heating, with an orange colour. Alizarin S decomposes on being heated strongly; splendid orange-red crystals of Alizarin are obtained by sublimation.

*Application.*—Alizarin S is not adapted for cotton dyeing. It is used in wool dyeing only, and in large quantities, as it dyes evenly. It is especially adapted for dyeing hard spun yarns and closely woven goods, since the colouring matter penetrates the material thoroughly. For the same reason the soluble Alizarin colours are employed in the Obermaier and similar dyeing machines. Alizarin S has the advantage of being a readily soluble powder, whereas the insoluble pastes are liable to dry up and to lose thereby colouring power. In dyeing, no untinned copper vessels should be used, since copper has a dulling effect on the colour; this may, however, be remedied by adding tin crystals, or a little ammonium sulphocyanide.

Alizarin S produces with aluminium a brighter scarlet than ordinary Alizarin; with chromium a good, but somewhat light, maroon; with iron a deep violet; and with stannic oxide a fine orange-yellow. For a full shade 2 to 4 per cent. of colour is required.

Goods to be dyed with Alizarin S in conjunction with alumina are mordanted exactly as prescribed for ordinary Alizarin with aluminium sulphate. The dye-bath is prepared with the required amount of Alizarin S and with 500 grms. (8 ozs.) of calcium acetate, 250 grms. (4 ozs.) of neutral soap, and 125 grms. (2 ozs.) of tannic acid for each kg. (lb.) of Alizarin S employed. The goods are introduced into the cold bath, which is heated to the boil in the course of forty-five minutes; after one hour boiling, 3 parts of acetic acid for each 1,000 parts of the dye-liquor are added, and the boiling is continued for half an hour. Colours are thus obtained which are very fast to light and milling. To obtain brighter colours some stannous chloride is added either to the mordanting or to the dye bath; in the latter case, the quantity is 10 to 20 per cent. of this salt (of the weight of the Alizarin S). If Alizarin S is combined with ordinary Alizarin, only so much acetic acid is added as is required by the former.

Alizarin S is dyed with chromium mordants exactly like ordinary Alizarin, and yields extremely fast claret to maroon shades.

Iron, tin, and other mordants are of no practical importance for the application of this dyestuff.

Alizarin S is especially adapted for dyeing by the "single-bath" method, owing to the solubility of the colour-lake; it is then dyed exactly as with

ordinary Alizarin. The colour produced in one bath, with the exception of that obtained on chromium mordants, is almost entirely removed by milling.

Alizarin S is also very well adapted to be dyed by "after-chroming" in combination with the acid chrome colours, and finds much application in this way. The wool is entered into the lukewarm bath prepared with the dyestuff and with 10 per cent. Glaubersalt and 2 per cent. sulphuric or oxalic acid, or 2 to 5 per cent. acetic acid; the liquor is heated within twenty to thirty minutes to the boil and boiled a half to three-quarters of an hour, when 1 to 2½ per cent. sulphuric acid or 2 to 5 per cent. acetic acid is added to exhaust the bath; then 1 to 3 per cent. bichromate is added and the bath is boiled again for twenty to thirty minutes.

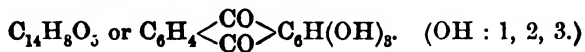
The methods described on p. 633 are also useful.

**PURPURIN. ALIZARIN No. 6.**

This dyestuff has already been described under Alizarin (p. 577).

*Application.*—Purpurin is very little used, as it is a very expensive dyestuff, and can be replaced at a lower cost by Alizarin G. It is dyed exactly as with Alizarin, and yields shades similar to Alizarin G. It is not so fast to light as Alizarin.

**ANTHRACENE BROWN (ANTHRAGALLOL, ALIZARIN BROWN)**  
(B.A.S.F., M.L.B., Bayer, British Alizarin Co.).



Anthracene brown is obtained by the condensation of benzoic and gallic acids, with the aid of sulphuric acid. It is a trioxyanthraquinone isomeric with the purpurins.

Commercial Anthracene brown forms a dark brown paste (20 per cent.) which is insoluble in water, but soluble in caustic alkalis. It dissolves in ammonia with a brown, and in caustic soda with a bluish-green colour; in these solutions a brownish precipitate is produced by hydrochloric acid. Anthracene brown dissolves in concentrated sulphuric acid with a brown-red colour; the solution gives, on diluting, a brownish flocculent precipitate.

Anthracene brown is also sold as a dark brown powder.

*Application.*—Anthracene brown is a very fast dyestuff. It yields with chromium mordants from light drab to dark brown shades with a yellowish bloom of excellent fastness to light, milling, acids, alkalies, &c. It produces on aluminium a light brown, on stannous oxide a red brown, on iron a blackish-brown, and on copper mordants a serviceable chestnut-brown shade; but the chromium colours only are of any importance.

*Cotton.*—Anthracene brown is used but little for cotton dyeing (except in calico-printing). It is dyed on aluminium and chromium mordants by the methods described in the beginning of this chapter (pp. 565 to 567).

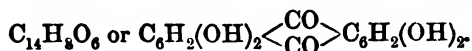
*Wool.*—Anthracene brown is dyed on wool with chromium mordants by the general methods described on p. 568. 1 per cent. of dyestuff in paste form gives a light drab, 10 to 20 per cent. a full reddish-brown shade of great fastness. With very dark shades it is well to add to the exhausted dye-bath ½ per cent. bichromate, and to continue boiling for half an hour. The single-bath method does not give satisfactory results with Anthracene brown.

*Silk.*—For methods of dyeing see p. 570. 25 per cent. of Anthracene brown (paste) gives a medium brown on aluminium, a full brown on chromium mordants.

*Anthracene brown in powder* is applied as follows:—The dyestuff is dissolved in water and the colour-solution is added to the dye-bath. The wool previously mordanted with bichromate in the usual manner is introduced into the cold bath, the temperature is raised in the space of half an hour

to 60°, and during the next hour a quantity of acetic acid equal in weight to the dyestuff employed is gradually added in small portions. The dyestuff is thus slowly precipitated from its solution and gradually fixed in the fibre. In the following thirty minutes the bath is brought to the boil, then 1 to 2 parts of acetic acid for each 1,000 parts of dye-liquor are added, and the boiling is continued for two hours.

**ALIZARIN BORDEAUX B (Bayer). ALIZARIN CYANIN 3 R.**



Alizarin bordeaux, in its chemically pure form marketed as Alizarin cyanin 3 R and chemically named quinalizarin, is 1 : 2 : 5 : 8 tetraoxyanthraquinone and is produced by treating Alizarin with a great excess of fuming sulphuric acid (70 per cent. anhydride) at the ordinary temperature. Commercial Alizarin bordeaux B forms a brown-red paste insoluble in water. It dissolves in caustic soda with a red-violet colour; in this solution a brown-red precipitate is formed by hydrochloric acid. Alizarin bordeaux dissolves in concentrated sulphuric acid with a blue-violet colour; the diluted solution gives a brown-red precipitate.

*Alizarin bordeaux G and G G*, the more yellowish brands, are mixtures of Alizarin bordeaux B and Alizarin.

*Application.*—Alizarin bordeaux B or Alizarin cyanin 3 R gives, with metallic mordants, shades which are invariably much bluer than the corresponding Alizarin shades. It gives a bluish-claret shade on aluminium similar to the Alizarin chromium colour; on chromium it yields fine violet-blue and on iron black-violet tints. Alizarin bordeaux B should be dyed without coming in contact with copper or copper salts.

*Cotton.*—Alizarin bordeaux is dyed on aluminium mordants by the new Turkey-red method (No. IV.) (p. 591); on chromium mordants by the general methods given in the introduction to this chapter (p. 566). An addition of calcium or magnesium salts to the dye-bath makes the bluish shades obtained on chromium mordant redder. The shades are very fast to light and soap, acids, &c., and very valuable for dyeing and calico-printing. Alizarin bordeaux is used extensively for the production of fast claret shades by the Alizarin red process (p. 591).

*Wool.*—Alizarin bordeaux is not used very extensively in wool-dyeing. Aluminium mordants are applicable. But more generally chromium mordants are used. The mordanting with chromic salts seems to be more suitable than that with bichromate;\* but usually bichromate is used in the usual manner for mordanting, care being taken to reduce the bichromate well by reducing assistants, such as tartar, lactic, or formic acid (see p. 256). Sulphuric acid is not a suitable assistant. The dyeing is carried out as with the other Alizarin colours (p. 568). The colour which, in the beginning, appears reddish, only by continued boiling acquires its fine bluish shade, a much more reddish violet-blue being obtained on bichromate than on chromium fluoride. The colours are very fast to light, milling, acids, alkalies, &c.

The *single-bath method* also gives excellent results; the shades become brighter, but less full; 4 to 6 per cent. of chromium fluoride and the required amount of dyestuff are added to the bath which is slowly heated to the boil and kept boiling for one and a-half to two hours; chromium fluoride may be added during the dyeing without any bad effects.

*Silk.*—Alizarin bordeaux may be dyed on silk mordanted with aluminium or chromium mordants according to the general methods (p. 570). On

\* *Journ. Soc. Dyers and Col.*, 1891, p. 121.

aluminium red-violet and on chromium blue-violet shades are obtained. A full shade requires about 30 per cent. of dyestuff.

**BRILLIANT ALIZARIN BORDEAUX R** (Bayer) is 1 : 2 : 5 trioxyanthraquinone.

*Application and Properties.*—Same as Alizarin bordeaux. The shade is similar to that of Alizarin bordeaux G, but considerably brighter.

**ALIZARIN CYANIN** (Bayer).

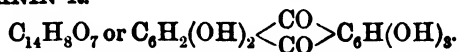
Under the denomination of *Alizarin cyanin* a great number of derivatives of anthraquinone are furnished to the trade, such as polyoxyanthraquinones, aminopolyoxyanthraquinones, products of the condensation of polyoxyanthraquinones with phenols, phenol carboxylic acids, amino-derivatives of such products, or sulphonic acids of the various kinds of compounds.

Some of the Alizarin cyanin brands are identical with some brands of Anthracene blue (see below).

The most important brands of Alizarin cyanin are 3 R, R, R extra, WR R, WR B, R R, G extra, G G, W D, W S, W R S, B B S, and Brilliant Alizarin cyanin G and 3 G.

**ALIZARIN CYANIN 3 R**, see Alizarin bordeaux B (p. 603).

**ALIZARIN CYANIN R.**



Alizarin cyanin R is chiefly 1 : 2 : 4 : 5 : 8 pentaoxanthraquinone, and is prepared by heating Alizarin bordeaux with manganese dioxide and sulphuric acid or with arsenic acid.

The commercial product forms a dark brown paste, insoluble in water. It dissolves in caustic soda with a blue colour, and is thrown down from this solution by hydrochloric acid as a brown precipitate. Alizarin cyanin R dissolves in concentrated sulphuric acid with a blue colour and a red fluorescence; on diluting, this solution yields a dark brown precipitate.

**ALIZARIN CYANIN G.**

This dyestuff is obtained by the action of ammonia on an intermediate product which is formed during the oxidation of Alizarin bordeaux to Alizarin cyanin R. The composition of the substance is not known.

The commercial product is a black paste, insoluble in water, but soluble in caustic soda with a green-blue colour. From this solution a dark precipitate is thrown down by hydrochloric acid. In concentrated sulphuric acid Alizarin cyanin G dissolves with a red colour; the solution yields a dark precipitate on diluting with water.

In addition to these brands of *Alizarin cyanin* a great number of others (see above) are in the market, which show similar properties.

*Application.*—The Alizarin cyanins dye from reddish-blue to greenish-blue shades on chrome mordants, and on alumina mordants red-violet to violet-blue shades. They are generally dyed on chrome mordants, and on alumina mordants chiefly for shading other Alizarin colours or for calico-printing. They possess excellent fastness to light, which is even superior to that of Alizarin blue, while the fastness to milling is not quite as good. The Alizarin cyanins also level better and are less disposed to rubbing than Alizarin blue, and for this reason they are used very much in wool dyeing, and especially so for piece dyeing. The dyestuffs are slightly sensitive to copper, and are best dyed in wooden vats with lead steam pipes.

Cotton is dyed with the Alizarin cyanins according to the general methods indicated on p. 565. An addition of calcium or magnesium salts makes the shades more reddish and intense. The colours on chrome are very fast to soap, those on alumina not quite so good; all the colours are very fast to light, alkalis, and acids.

Wool is dyed as with Alizarin bordeaux (p. 603). The reddish brands become more greenish by being passed, after dyeing, through ammonia. The best levelling brands are 3 R, 2 R, and N S, and the brands G G and W R R are best in fastness to milling. In order to obtain colours which entirely resist severe milling it is best to treat the wool in the exhausted dye-bath with  $\frac{1}{2}$  to 1 per cent. bichromate.

Alizarin cyanin G G, W R R, R R, N S, and B B S may be dyed by the after-chroming method. Prepare the bath with the colouring matter, 2 to 4 per cent. acetic acid and 10 to 20 per cent. Glaubersalt, enter the non-mordanted wool at 50° to 60°, bring slowly to the boil, and, if the bath is not perfectly exhausted, add a little acetic or sulphuric acid. Then chrome in the same or in a fresh bath for thirty to forty minutes at the simmer with about a half to two-thirds the quantities of bichromate or chromium fluoride corresponding to the weight of dry dyestuff.

The colours are very fast to light, milling, alkalis, and acids.

Silk is dyed a very fast blue after previous mordanting with chrome (p. 570).

**ALIZARIN CYCLAMIN R** (Bayer) is a hexaoxyanthraquinone (OH : 1, 2, 4, 5, 6, 8) which also belongs to the group of Alizarin cyanins. It yields on aluminium mordant beautiful red-violets of excellent fastness to light and washing, and is used for printing, especially for upholstery cloths.

**ALIZARIN CYANIN W R S** (Bayer).

This is a sulphonic acid of the Alizarin cyanin group.

Brown powder; aqueous solution, dark violet-red; HCl, red solution and readily soluble precipitate; NaOH, soluble blue-violet precipitate; solution in  $H_2SO_4$ , violet; on diluting, red.

*Application.*—Alizarin cyanin W R S is dyed on wool by the after-chroming method, and serves chiefly for yarn and piece dyeing. The material is dyed one hour at the boil with the addition of 2 to 3 per cent. oxalic acid, and then treated in the exhausted dye-bath at the boil with 2 to 4 per cent. chromium fluoride. A reddish-blue very fast to light, acids, and alkalis, and fairly fast to milling, is obtained in this way.

**ANTHRACENE BLUE (B.A.S.F.).**

Anthracene blue is found in commerce in a great number of brands which are chiefly obtained by the action of fuming sulphuric acid containing varying proportions of sulphuric anhydride on 1 : 5 dinitroanthraquinone, the acid acting either in presence or in absence of reducing agents. Anthracene blue W G new is produced by the action of caustic soda and ammonia on Anthracene blue in a closed vessel, and the most greenish brands W G G and W G G extra by heating dinitroanthraquinone with fuming sulphuric acid, sulphur, and boric acid. The products appear to be hydroxy or amino-hydroxy derivatives of Alizarin which closely resemble the Alizarin cyanins or are identical with them. They are marketed as dark pastes or powders; the latter are the sodium salts and dissolve in water with dark red-violet to dark blue colours; hydrochloric acid produces dark brown or violet precipitates; caustic soda produces blue solutions and soluble precipitates. Solution in  $H_2SO_4$ , violet-blue (S W R) or violet (S W B) or red-violet (S W G) or brown (S W G G); on diluting, brown-red or red solutions and brown-red or red-brown precipitates.

*Application and Properties.*—Same as Alizarin cyanin. The more reddish brands like W R R, W R, and W B correspond to the redder cyanins, and the more greenish brands like W G, W G new, W G extra, and W G G extra to the greener cyanins. Well-covered shades are produced with Anthracene blue W N and Anthracene dark blue W. Anthracene blue W G and W G G may be dyed by the one-bath method like the brand S W X (see below). The sodium salts which are soluble in water are denominated by

the letter S—*e.g.*, Anthracene blue SWB. The S brands are usually eight times as strong as the corresponding pastes; Anthracene blue SWN is only five and a third times as strong, and Anthracene dark blue SW only four times. The brands intended for cotton dyeing are denominated without the letter W.

**ANTHRACENE BLUE SWX** (B.A.S.F.) is very similar to Alizarin cyanin WRS (p. 605), and applied in the same way.

**BRILLIANT ALIZARIN CYANIN G and 3 G** (Bayer).

These two brands belong chemically to the group of the preceding Alizarin cyanins and Anthracene blues, but are distinguished by their tinctorial properties, as they can be dyed very well on wool in acid baths like the acid colours.

Brownish-blue paste or powder; aqueous solution, violet; HCl, red-violet precipitate, sparingly soluble; NaOH, blue solution; solution in  $H_2SO_4$ , yellowish-brown; on diluting, red-violet.

*Application.*—Brilliant alizarin cyanin is dyed on wool either direct in an acid bath or in combination with chrome mordants, both on chromed wool or after-treated with bichromate. Dyed direct it yields fine reddish-blue shades of excellent fastness to light and not sensitive to dilute acids, but moderately fast to washing; the dyeings become lighter and more greenish by the action of soap or alkalis, and on pieces water drops produce a rim or spot, as is the case with many Alizarins when dyed direct. By a subsequent treatment with chromium fluoride the colours become slightly more greenish and with bichromate considerably more greenish. By a heavy treatment with bichromate (2 to 3 per cent.) and sulphuric or oxalic acid the colours are destroyed. Greenish-blue shades are also produced on wool mordanted with bichromate and reducing assistants (tartar, &c.). The colours obtained with chrome—either by subsequent or by previous chroming—are very fast to light, acids, alkalis, washing, and also very satisfactory to milling. Brilliant alizarin cyanin G dyes slightly more reddish shades than the “3 G” brand.

**ALIZARIN MAROON** (B.A.S.F.).

Alizarin maroon is  $\beta$ -amino-alizarin, the composition of which is  $C_{14}H_9O_4N$ , or  $C_{14}H_5O_2(OH)_2NH_2$ , mixed with some amino-purpurin. It is produced by the reduction of the nitration product of Alizarin in sulphuric acid solution.

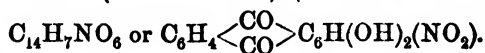
Alizarin maroon is sold as a brown paste (20 per cent.), insoluble in water, but soluble in caustic soda with a violet colour; the alkaline solution gives, on diluting with water, a brown precipitate. The solution of the dyestuff in concentrated sulphuric acid is crimson-red and gives a brown precipitate when diluted. Alizarin maroon is not quite so fast as most of the other Alizarin dyestuffs. It is dyed on cotton, wool, and silk by the general methods used for the mordant colours (p. 564, *et seq.*), and may be dyed with aluminium mordants like Alizarin on cotton (p. 591), and on wool (p. 599). On aluminium it gives garnet, on chromium maroon shades.

**ALIZARIN GARNET R (M.L.B.). ALIZARIN CARDINAL** (Bayer).

This dyestuff is obtained by reduction of alpha-nitroalizarin, and is isomeric with Alizarin maroon.

Red-brown paste, difficultly soluble with a dirty pink colour in water; it is soluble in caustic soda lye with a ruby-red colour, and precipitated from this solution by hydrochloric acid. Solution in  $H_2SO_4$ , orange-brown; on diluting, red precipitate.

*Application.*—Alizarin garnet or cardinal is dyed by the ordinary methods (p. 564, *et seq.*), and yields on alumina mordants, very bluish-red; on chrome mordants, claret shades of the same fastness as those produced with Alizarin maroon. It is principally used for shading Alizarin in cotton dyeing, and especially so in calico-printing.

**ALIZARIN ORANGE (A or N or AO) (NITRO-ALIZARIN).**

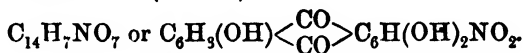
Alizarin orange or beta-nitroalizarin is formed by the action of nitrous or nitric acid on Alizarin. The dyestuff is sold either as a brownish-yellow paste (with 20 per cent. of colour), insoluble in water; or as a brown-orange powder—in the form of the acid sodium salt—which dissolves in water with a claret-red colour. The powder has four or five times more tinctorial power than the paste. Both the paste and the powder dissolve in very dilute caustic soda with a crimson colour; an excess of caustic soda causes the solutions to yield a claret-red flocculent precipitate. The alkaline solutions yield orange precipitates on addition of hydrochloric acid. The solution in concentrated sulphuric acid is orange; on diluting with water a yellow precipitate is obtained. Reducing agents transform the nitro-alizarin into the amido-alizarin, which dissolves in caustic soda with an intense blue colour.

*Application.*—Alizarin orange produces, with aluminium, orange; with chromium, dull brownish-red; with iron, purplish-brown; and with copper, brown-red shades. Stannic oxide gives a light orange, while stannous oxide has a reducing action on the colour.

Alizarin orange gives very fast shades. It is used on cotton, wool, and silk as already stated in the beginning of this chapter (p. 564, *et seq.*). The powder is dyed on wool with aluminium mordant like ordinary Alizarin (p. 599), with chromium mordant like Anthracene brown (powder) (p. 602). Both the paste and the powder may be dyed on wool by the after-chroming method—i.e., first dyeing in the acid bath, and subsequently chroming with bichromate.

Silk requires about 25 per cent. of the paste for a full shade.

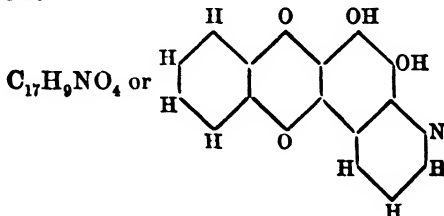
Alizarin orange is principally used for shading other Alizarin colours in wool dyeing and in calico-printing.

**ALIZARIN ORANGE G (M.L.B.).**

Alizarin orange G is beta-nitroflavopurpurin, produced by the action of nitric acid on flavopurpurin.

Yellow, difficultly soluble paste; aqueous solution, brownish-red; HCl, in the cold no change; on heating, a part is dissolved with a yellowish-green colour; NaOH, dark red solution; solution in  $H_2SO_4$ , brown-red; on diluting, brown-yellow precipitate.

*Application.*—Same as ordinary Alizarin orange (see above). The shade of Alizarin orange G is much more yellowish than that of the older brand and brighter. The colour possesses good fastness to light, washing, milling, alkalis, acids, chlorine, and stoving.

**ALIZARIN BLUE.**

Alizarin blue is dioxanthraquinone-quinoline; it is produced by heating beta-nitroalizarin (Alizarin orange) or beta-aminoalizarin with glycerin and



sulphuric acid when, by a complicated reaction, the new dyestuff is formed. Alizarin blue is sold as a violet-blue paste of crystalline leaflets with a coppery lustre, insoluble in water, or in the form of the sodium salt as a soluble powder (Alizarin blue X A or W A or D N W); it dissolves in caustic soda with a green-blue colour; an excess of alkali precipitates the colour; hydrochloric acid makes the alkaline solution reddish-yellow. The solution in concentrated sulphuric acid is crimson, which colour changes to a pale orange-yellow when water is added. Alizarin blue forms a lime-lake insoluble in water; the presence of acetic acid prevents the formation of this lake.

Alizarin blue contains the two hydroxyl-groups of Alizarin, and is, therefore, a weak acid; on the other hand, it is a derivative of the base "quinoline"; hence it possesses a weak basic character, and combines with acids to form unstable salts. Alizarin blue forms with calcium, barium, zinc, and iron, greenish-blue; with nickel and chromium, blue; with aluminium, purplish-blue; and with tin, purplish lakes. Thus, it does not show distinctly the polygenetic character of the other Alizarin colours, and also differs from them in dyeing unmordanted fibres a greenish-blue colour. Alizarin blue in alkaline solution is reduced by zinc dust, and yields a red liquid which, when exposed to the air, resumes its original colour, forming a vat like indigo. Cotton and wool can be dyed in this vat.

*Application.*—Alizarin blue is almost exclusively used in combination with chromium mordants. When this method was first introduced the insufficient solubility of the commercial product prevented its general application. But later on it has been furnished in a finely-divided form, also as the soluble sodium salt (see above), and as the soluble bisulphite compound (see Alizarin blue S), and it is now used in considerable quantities, although in wool dyeing it has been replaced to a great extent by the Alizarin cyanins or Anthracene blues and the acid chrome colours. Alizarin blue forms insoluble lime-lakes; hence calcareous water must not be used, or, if used, must be corrected with acetic acid.

Cotton has been dyed with Alizarin blue by the vat-dyeing method described above; after dyeing, the goods were passed through solutions of chloride of lime or bichromate. But this method has been abandoned, as the colours are too fugitive. It is now always dyed on chromium mordants, according to the general methods stated on p. 566, and thus yields very fast colours. After treatment with sodium bisulphite, Alizarin blue may be used in the same way as Alizarin blue S on chromium mordant. It is only the chemically pure Alizarin blue that is fast to bleaching—e.g., Alizarin blue F paste or S B powder (M.L.B.). The yarn is oiled well with rancid Gallipoli oil or Turkey-red oil, and then mordanted overnight in a bath of  $\frac{1}{2}$  lb. tannic acid per 10 gallons of water (sumach is not so well adapted, since, after bleaching, the blue turns greener). If Gallipoli oil is used the tannin may be dispensed with. The yarn is then mordanted for twelve hours in a cold bath of chromium chloride 18° Tw., steeped and washed, and dyed. For dyeing 100 lbs. of yarn, 15 lbs. Alizarin blue F, 3 galls. acetic acid 8° Tw.,  $1\frac{1}{2}$  galls. ammonia 25 per cent., and  $2\frac{1}{2}$  ozs. tannic acid; or 5 lbs. Alizarin blue S B, 5 lbs. acetic acid 8° Tw., and  $2\frac{1}{2}$  ozs. tannic acid are used; dye one hour cold, heat within one hour gradually to the boil, and boil three-quarters of an hour. Wash, hydro-extract, steam for two hours at 14 to 21 lbs. pressure, and soap at the boil with  $\frac{1}{2}$  to 1 oz. soap per gallon.

Wool is mordanted with bichromate of potash, or with chromium fluoride, and dyed by the ordinary methods stated on p. 568. But the use of Alizarin blue S is preferable. The sodium salt is used in machine dyeing for dyeing worsted tops.

Alizarin blue dyed carefully on mordanted material equals Alizarin blue S in fastness.

**ALIZARIN BLUE S** (B.A.S.F., Bayer, M.L.B., British Alizarin Co.).  
 $C_{17}H_9NO_4 + 2NaHSO_3$ .

Alizarin blue S is a compound of ordinary Alizarin blue with sodium bisulphite; it is formed when Alizarin blue is mixed with a strong solution of sodium bisulphite, and allowed to stand for about two weeks.

Alizarin blue S comes into the market either as a dark purple powder, easily soluble in water with a brown-red colour, or as a strong solution (20 per cent.). The aqueous solution is turned blue-green by caustic soda, and reddish-yellow by hydrochloric acid. Alizarin blue S dissolves in concentrated sulphuric acid with a brown colour; the solution becomes pale orange on diluting with water. The bisulphite compound is resolved into insoluble Alizarin blue and bisulphite, when its aqueous solution is heated to about 70°; strong acids, alkalies, or alkaline carbonates have a similar effect. Acetic or tartaric acid do not affect the compound, nor does Alizarin blue S form lakes with the acetates of calcium and chromium at the ordinary temperatures.

*Application.*—Alizarin blue S decomposes (as stated above) in solution when heated above 70°. Hence, when dissolving the dyestuff the water must not be too hot, and in dyeing the temperature must not be raised above 70° before the colouring matter has been well taken up by the fibre; if the temperature rises too high there will be unevenness and loss of dyestuff and the colour rubs. Most of the colouring matter is absorbed between 55° and 65°; on heating above 70° the bisulphite compound is decomposed, and the Alizarin blue gradually combines with the mordant in the fibre with the formation of an insoluble colour-lake.

Calcareous water is acidulated with acetic acid (about 1 part of acetic acid for 1,000 parts of soft water and more for hard water). The use of calcium salts in dyeing with Alizarin blue has no advantage; on the contrary, it makes the shade decidedly duller.

**Cotton.**—Alizarin blue S is dyed on cotton with chromium mordants by two methods.

(1) *Mordanting and Dyeing Method.*—The cotton is mordanted with chromium oxide, with or without previous oiling, and dyed as with the other mordant colours (p. 566); no calcium acetate is added to the bath.

(2) *Single-Bath or Padding Method.*—1 kg. (10 lbs.) of Alizarin blue S (powder) is dissolved in 8 litres (8 galls.) of cold water (preferably distilled water), and when all is dissolved 1 litre (1 gall.) of chromium acetate (32° Tw.) is added. Or 3 kgs. (30 lbs.) of Alizarin blue S (paste), 6 litres (6 galls.) of cold water, and 1 litre (1 gall.) of chromium acetate (32° Tw.) are dissolved in the same manner. The cotton material is steeped in this solution; for lighter shades weaker, for darker shades stronger solutions (or repeated steeping operations) are applied. The cotton when evenly saturated with the liquor is wrung out and dried at a temperature not exceeding 40°; after drying it is steamed for one hour at 8 lbs. pressure, or for two hours without pressure; finally, it is washed, soaped, and dried. By the steaming process the bisulphite-compound of Alizarin blue is decomposed and the insoluble chromium lake is formed.

Alizarin blue S on cotton is very fast to light and exceedingly fast to all other influences.

**Wool.**—Alizarin blue S has proved to be a valuable substitute for vat-indigo in wool dyeing, in which respect it is superior to most other wool dyestuffs. It is easily applied, and penetrates the fibre thoroughly; it is as fast to milling and soaping as indigo, while it has the decided advantage of not rubbing; on the other hand, it does not equal indigo in fastness to

light, and does not show the fine bloom of vat-indigo shades. Although Alizarin blue S is not quite so fast to light as indigo, the difference is not great for deep shades if mordanted and dyed in the right way, without too great an excess of mordant. Alizarin blue S is dyed on wool with chromium mordants only. For mordanting methods see p. 255; 3 per cent. of bichromate of potash, in combination with reducing assistants, gives very good results; the addition of sulphuric acid to the mordanting bath is not advisable. The chromed wool may be subsequently reduced with sodium bisulphite, or chromium salts (chromium fluoride, for instance) may be used.

The dyeing proceeds in a separate bath as usual; the single-bath method does not give satisfactory results. To obtain a good fast blue the bath must be slowly raised to boiling and maintained so until a pure shade is obtained (one to two hours). Alizarin blue S yields on wool deep indigo-blue shades, which are very fast to light and exceedingly fast to milling, scouring, and rubbing, and to dilute acids and alkalis.

Alizarin blue S is of great importance in wool dyeing, owing to its excellent fastness to milling, being in this respect superior to the Alizarin cyanins and Anthracene blues. It is, however, more difficult to dye, and is now principally used for self shades; for mixed shades it has been generally replaced by the above-named colours and the numerous blue acid chrome colours.

Silk can be dyed with Alizarin blue S in the same way as with the other Alizarin colours with the aid of chromium mordants (p. 570). 8 per cent. of Alizarin blue S (powder) is required for a full shade.

**ALIZARIN DARK BLUE S (B.A.S.F.)** is a special brand of Alizarin blue S, which dyes a dull reddish-blue, and is only suitable for dark shades. It is applied like Alizarin blue S, and possesses the same properties and equal fastness.

#### **ALIZARIN GREEN S (B.A.S.F.).**

Alizarin green is produced by the action of very strong fuming sulphuric acid on Alizarin blue, and is a mixture of tri- and tetra-oxyanthraquinone quinoline and their sulphonc acids.

The commercial article Alizarin green S is the bisulphite-compound, and resembles Alizarin blue S. It is a dark brown liquid, having a strong odour of sulphurous acid, and yields a blue precipitate on boiling (insoluble Alizarin green). The diluted aqueous solution is dark orange to reddish-brown; caustic soda makes the solution blue in the cold, but on boiling it produces a dark green precipitate; hydrochloric acid has no action in the cold, but on boiling it drives off sulphurous acid, and produces a dark precipitate.

Alizarin green—i.e., the substance obtained by the decomposition of the bisulphite compound—is dissolved by sulphuric acid with a dark blue-violet colour; on diluting, a reddish-brown precipitate is formed.

*Application.*—Alizarin green S yields a dull shade of green-blue with chromium mordants, and is applied to the various fibres exactly like Alizarin blue S. Very fine effects are obtained in light shades produced with chromium mordants on cotton, especially in calico-printing.

Alizarin green S is a very fast dyestuff.

#### **ALIZARIN INDIGO-BLUE S (B.A.S.F.).**

This dyestuff is obtained in the same way as Alizarin green S when Alizarin blue is heated with fuming sulphuric acid to 210°. It chiefly consists of penta-oxyanthraquinone quinoline and its sulphonc acid. The commercial product is also a bisulphite-compound. It forms a dark red-brown liquid, which becomes brown-red to cherry-red on dilution with water. Caustic soda turns the solution blue, and decomposes it on heating; hydrochloric acid has no action in the cold, but at the boiling temperature

sulphurous acid is driven off, and a dark blue precipitate is formed. This precipitate is dissolved by concentrated sulphuric acid with a blue colour; the solution gives a red-violet precipitate when diluted.

*Application.*—Alizarin indigo-blue S gives an indigo-blue shade with chromium mordants, and is dyed on the various fibres in exactly the same way as Alizarin blue S. The shades are very fast.

#### ALIZARIN GREEN S (M.L.B.).

This brand of Alizarin green is produced by heating alpha-aminoalizarin (Alizarin garnet, p. 606) with glycerin, nitrobenzene, and sulphuric acid. It is alpha-alizarin quinoline isomeric with Alizarin blue.

Red-brown paste or powder; aqueous solution, red-violet; HCl, soluble greenish-grey precipitate; NaOH, crimson-red solution; solution in H<sub>2</sub>SO<sub>4</sub>, crimson-red; on diluting, brown precipitate.

*Application.*—Alizarin green S is dyed on cotton or wool mordanted with chrome a not very bright, fairly bluish-green, which is very fast to light, washing, milling, alkalis, and acids. It is used for compound shades, principally in calico-printing.

#### ALIZARIN BLACK P and S (M.L.B.).

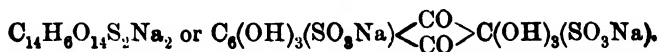
Alizarin black P is the quinoline of Flavopurpurin—i.e., an oxalizarin quinoline—and is obtained from Alizarin orange G (M.L.B.) in the same way as Alizarin blue is from ordinary Alizarin orange. Its bisulphite-compound is furnished to the trade as Alizarin black S.

*Alizarin Black P.*—Greyish-black, sparingly soluble, paste; solution in NaOH, greyish-green; on addition of HCl, brown precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, dark brown; on diluting, yellowish-brown precipitate.

*Alizarin Black S.*—Brownish-black paste, soluble with a brown colour, which otherwise gives the same reactions as the "P" brand.

*Application.*—Alizarin black P may be dyed on cotton or wool mordanted with chrome for the production of reddish-grey or compound shades. It finds its chief application in calico-printing, and still more so the "S" brand. The colours show good fastness.

#### ACID ALIZARIN BLUE B B and G R (M.L.B.).

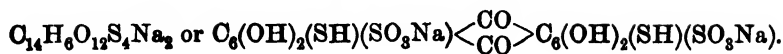


(OH) : 1, 3, 4, 5, 7, 8; (SO<sub>3</sub>Na) : 2, 6.

Acid alizarin blue is produced by boiling diaminoanthrachryson disulphonic acid with alkalis, and is the sodium salt of hexaoxyanthraquinone disulphonic acid. It is a derivative of Alizarin, whereas anthrachryson does not contain any hydroxyl groups in orthoposition to each other. The latter is 1 : 3 : 5 : 7 tetraoxyanthraquinone, which is obtained by heating symmetrical dioxybenzoic acid in sulphuric acid.

Brown powder; aqueous solution, red-violet; HCl, soluble red-violet precipitate; NaOH, blue solution and soluble blue precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, red-violet; on diluting, red or violet.

*Application.*—Acid alizarin blue is dyed on wool by the after-chroming method. It is dyed with the addition of 3 per cent. sulphuric acid and 10 to 50 per cent. Glaubersalt, and then developed in the same or in a separate bath by boiling for three-quarters to one and a-half hours with 2 to 5 per cent. chromium fluoride. Bichromate cannot be employed with this dyestuff. Acid alizarin blue B B dyes a fairly bright, slightly greenish-blue, and the brand G R a less bright dark blue. The colours are very fast to light, washing, milling, acids, and alkalis.

**ACID ALIZARIN GREEN B and G (M.L.B.).**

(OH) : 1, 3, 5, 7 ; (SH) : 4 and 8 ; (SO<sub>3</sub>Na) : 2 and 6.

Acid alizarin green G is produced by reducing dinitroanthrachryson disulphonic acid (obtained by sulphonation and nitration of anthrachryson, see *Acid alizarin blue*) with sodium sulphide in alkaline solution. It contains (in both benzene rings) a hydroxyl group and a SH group in orthoposition to each other, and in so far it corresponds to the original rule of Liebermann and Kostanecki.

Black powder ; aqueous solution, bluish-green ; HCl, blue solution ; NaOH, violet solution and soluble red-violet precipitate ; solution in H<sub>2</sub>SO<sub>4</sub>, violet ; on diluting, blue.

*Application.*—Same as Acid alizarin blue. Acid alizarin green, however, may be chromed either with chromium fluoride or with bichromate. It dyes fairly bright shades of green and good dark greens, which are very fast to light, washing, milling, acids, and alkalis.

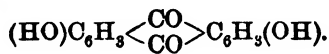
**ACID ALIZARIN GREY G (M.L.B.).**

Black powder ; aqueous solution, dark violet-blue ; HCl, dark violet precipitate ; NaOH, greener solution ; solution in H<sub>2</sub>SO<sub>4</sub>, dull brown-red ; on diluting, dark violet precipitate.

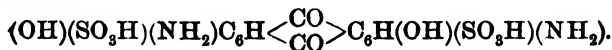
*Application.*—This dyestuff may be dyed on wool either direct in an acid bath, or in combination with chromium mordants. It levels very well, and yields direct a bluish-grey of very good fastness to light, dilute acids, and alkalis, and fairly fast to washing. On chromed wool similar shades of equal fastness and fairly good fastness to milling are produced. Dyed by the one-bath or after-chroming method, slightly duller shades of grey are obtained, which are very fast to light, milling, acids, and alkalis. Acid alizarin grey is not sensitive to copper, and, owing to its good levelling properties, it may be dyed as well on piece goods as on loose wool, slubbing, or yarns, both for greys and other mixed shades.

**ALIZARIN SAPHIROL B and S E (Bayer).**

Alizarin saphirol B is diaminoanthrarufin disulphonic acid, and the "S E" brand the corresponding monosulphonic acid. Anthrarufin is 1 : 5 dioxyanthraquinone,



*Alizarin saphirol B :*



(OH) : 1, 5 ; (SO<sub>3</sub>H) : 2, 6 ; (NH<sub>2</sub>) : 4, 8.

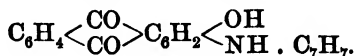
Greenish-black powder ; aqueous solution, blue ; HCl, redder solution and readily soluble precipitate ; NaOH, little change ; solution in H<sub>2</sub>SO<sub>4</sub>, yellow ; on diluting, at first red, then violet, and finally blue.

*Application.*—Alizarin saphirol is not a mordant dyestuff proper, although it may be dyed on chromed wool. It finds its chief application as an acid dyestuff on wool, being dyed with the addition of sulphuric acid and Glaubersalt, according to Method I., p. 513. It dyes very level, and yields a very bright and slightly greenish-blue of excellent fastness to light, which even in pale shades is very good. It is not sensitive to dilute acids, but not very fast to soap, alkalis, or water, especially the "B" brand, which easily shows water marks by falling water drops, whereas Alizarin saphirol S E is.

much better in this respect. On chromed wool more greenish and duller shades are obtained, of good fastness to light, milling, water, and alkalis.

**ALIZARIN IRISOL R** (Bayer).

This is the sulphonic acid of (1) oxy (4) paratolylaminoanthraquinone,

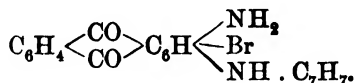


Reddish-blue powder or paste; aqueous solution, reddish-blue; HCl, reddish-blue precipitate; NaOH, greenish-blue precipitate; solution in  $\text{H}_2\text{SO}_4$ , bright blue; on diluting, reddish-blue precipitate.

*Application.*—Alizarin irisol R is applied exactly like Alizarin saphirol, and possesses the same fastness; the fastness to water and alkalis is fairly good. It dyes direct on wool bright violet shades, and especially useful violet, lilac, and heliotrope shades fast to light. For dyeing with chromium mordants it is not very suitable, being altered too much by the latter.

**ALIZARIN SKY BLUE B** (Bayer).

This is the sulphonic acid of (1) amino- (2) bromo- (4) *p* tolylamino-anthraquinone,

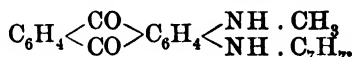


Reddish-blue powder; aqueous solution, blue, precipitating small coppery crystals; HCl, blue precipitate; NaOH, greenish-blue precipitate; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, at first red, then blue precipitate.

*Application.*—Alizarin sky blue B is also applied exactly like Alizarin saphirol, and possesses the same fastness; the fastness to water and alkalis is fairly good. It dyes pure shades of blue less greenish than those of Alizarin saphirol, which may be fixed without considerable alteration by subsequent chroming with bichromate. Although not a mordant dyestuff proper, Alizarin sky blue B may be dyed quite well on chromed wool for shading purposes.

**ALIZARIN ASTROL B** (Bayer).

Sulphonic acid of (1) methylamino- (4) *p* tolylamino-anthraquinone,

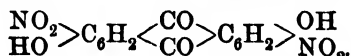


Blue powder; aqueous solution, greenish-blue; HCl, reddish precipitate; NaOH, greenish-blue precipitate; solution in  $\text{H}_2\text{SO}_4$ , blue; on diluting, magenta-red and reddish precipitate.

*Application.*—Alizarin astrol B is also a very good levelling dyestuff for wool, of the same tinctorial properties and fastness as the preceding dyestuffs. It dyes more greenish blues than Alizarin saphirol, and is suitable for blue, green, &c. It is not altered much by chroming, and may be used for shading acid chrome colours or mordant colours. It is also recommended for dyeing mode shades fast to light on silk.

**ALIZARIN EMERALDOL G** (Bayer).

This dyestuff, the constitution of which has not yet been determined, is obtained by the action of alkaline sulphides on the disulphonic acid of *p* dinitroanthrarufin (anthrarufin = 1 : 5 dioxyanthraquinone),



Dark blue powder; aqueous solution, bluish-green; HCl, bluish-green precipitate; NaOH, solution much greener, and soluble precipitate; solution

in  $H_2SO_4$ , yellowish-red; on diluting, at first more bluish and then bluish-green precipitate.

*Application.*—Alizarin emeraldol G is a levelling dyestuff for wool which has the same tinctorial properties and fastness as the preceding dyestuffs. It dyes bright blue-green shades which, by chroming with chromium fluoride, become greener, and with bichromate, olive. It levels better than Alizarin cyanine green (see below), and is preferable to this dyestuff for piece goods requiring good levelling.

**ALIZARIN CYANINE GREEN G EXTRA (Bayer).**

This is the sulphonic acid of 1 : 4 *p* tolylaminoanthraquinone, produced by the action of *p* toluidine on quinizarin (1 : 4 dioxyanthraquinone) and sulphonation of the product. It was the first anthraquinone dyestuff obtained which does not contain a hydroxyl group.

Bluish-green powder; aqueous solution, bluish-green; HCl, dark soluble precipitate; NaOH, dark soluble precipitate; solution in  $H_2SO_4$ , dull reddish-blue; on diluting, bluish-green.

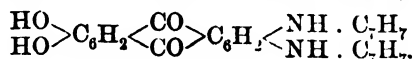
*Application.*—Alizarin cyanin green is principally dyed on wool, either direct or in combination with chrome mordants. When dyed direct with the addition of acetic acid and sodium sulphate, it yields a bright bluish-green of excellent fastness to light, but not very fast to washing; the fastness to dilute acids and alkalis is good. The shade becomes slightly duller by subsequent chroming with chromium fluoride, and more so by bichromate; it thus becomes much faster to milling, but only fast enough for light milling; the fastness to light of the chromed colour is excellent. The same colour but not quite as fast to milling, is obtained on chromed wool. On cotton mordanted with alumina, a delicate blue-green; and with chromium mordant, less bright shades of excellent fastness to light are produced.

**ALIZARIN CYANINE GREEN K and E (Bayer)** are very similar to the preceding brand. "K" levels better, "E" is less bright in shade.

**ALIZARIN CYANINE GREEN 3 G (Bayer)** is an oxy-derivative of the brand G extra of yellowish-green shade. The hydroxyl group does not affect the resistance of the product to alkali nor to chroming, but makes it suitable to be printed in combination with chromium mordant on cotton.

**ALIZARIN VIRIDINE (Bayer).**

This is a sulphonic acid of (1 : 4) di-*p*-tolylamino (5 : 8) dioxyanthraquinone,



Dark green paste or powder; aqueous solution, bluish-green; HCl, no change; NaOH, bluer; solution in  $H_2SO_4$ , blue-green; on diluting, no change.

*Application.*—Alizarin viridine, owing to the two hydroxyl groups it contains, has the properties of a true mordant dyestuff. It is principally used in *calico-printing*, and yields in combination with chromium salts fine green shades of excellent fastness to light and washing. On unmordanted wool, yellowish-green shades; and on chromed wool, bluish-green shades of very good fastness to light are produced.

**ALIZARIN RUBINOL R (Bayer)** is a new product, also belonging to the group of arylaminoanthraquinone dyestuffs, the exact constitution of which has not yet been published.

Bluish-red powder, fairly soluble in water; aqueous solution, violet-red; HCl, red-violet precipitate; NaOH, violet precipitate; solution in  $H_2SO_4$ , magenta-red; on diluting, red-violet precipitate.

*Application.*—Alizarin rubinol R is an acid dyestuff for wool and, on prolonged boiling, levels well, and yielding bluish-red shades of excellent fastness to light, it is also fairly fast to washing, and good to acids and

alkalies. It is dyed with sulphuric acid by the first method (p. 513), and may also be subsequently treated with bichromate, although its fastness is not materially enhanced by such treatment. A good shade is also obtained on wool in a neutral bath. In dyeing silk-wool unions in an acid bath both fibres are dyed a uniform shade, and cotton threads are left unstained.

**ALIZARIN HELIOTROPE R** (Bayer) is a dioxyphenylaminoanthraquinone.

Dark reddish-brown paste, soluble in much water; aqueous solution, crimson-red; HCl, flocculent red-brown precipitate; NaOH, little change; solution in  $H_2SO_4$ , bluish magenta-red; on diluting, yellowish-red solution and flocculent precipitate.

*Application.*—Alizarin heliotrope R gives on cotton in combination with alumina mordants very bright heliotrope shades which, however, are not so fast to light or washing as usual with the Alizarins, and it is, therefore, used only to a limited extent, principally in calico-printing.

**ALIZARIN HELIOTROPE B B** is similar, and produces slightly bluer shades of heliotrope.

**ALIZARIN BLUE-BLACK B** (Bayer).

This dyestuff chemically belongs to the same group of Alizarin colours, and is also a sulphonated product of the condensation of an Alizarin with an amino-compound of the aromatic series.

Black-brown powder; aqueous solution, dark violet; HCl, soluble red-violet precipitate; NaOH, violet-blue solution; solution in  $H_2SO_4$ , violet; on diluting, dull red-violet.

*Application.*—Alizarin blue-black B is used on wool in combination with chromium mordants, either on chromed wool or more frequently by the after-chroming method, but not for direct shades. It produces greys and blue-blacks, and serves chiefly for the production of greys and for shading or saddening mixed colours. It dyes very level, and yields colours of excellent fastness to light, milling, acids, and alkalies. The colours dyed in an acid bath and subsequently chromed are fuller in shade and faster to milling than those dyed on chromed wool.

**ALIZARIN BLUE-BLACK 3 B** (Bayer) and **ALIZARIN FAST GREY T** (Bayer) are analogous to the preceding brand. Alizarin blue-black 3 B dyes slightly more bluish, and Alizarin fast grey T more yellowish and duller shades of the same fastness as Alizarin blue-black B.

**CYANANTHROL** (B.A.S.F.).

Bluish-grey to blue powder; aqueous solution, blue; HCl, bluish-red to claret-red; NaOH, soluble azure blue precipitate; solution in  $H_2SO_4$ , ruby-red; on diluting, blue-violet precipitate.

*Application.*—Cyananthrol is furnished to the trade in various brands, R, R B, R A, B A, and B G A. It is used in wool dyeing in an acid bath, and levels fairly well. It dyes bright blues of excellent fastness to light, good fastness to acids, and fairly good fastness to washing and alkalies. By chroming, the shades are dulled; although it thereby becomes faster to milling, it is not a mordant dyestuff proper, and is chiefly used as a direct colour on yarn and piece goods for blues and mixed shades fast to light.

**ANTHRAQUINONE VIOLET** (B.A.S.F.).

Sulphonic acid of di-*p*-tolylamino anthraquinone produced by condensation of dinitroanthraquinone with *p* toluidine and sulphonation of the product.

Blue-violet powder; aqueous solution, red-violet; HCl, violet precipitate; NaOH, violet precipitate; solution in  $H_2SO_4$ , brown; on diluting, red-violet.

*Application.*—Anthraquinone violet dyes on wool fairly bright bluish-red shades and is dyed either direct in an acid bath or in combination with chromium mordants. The fastness to light, even of pale shades, is excellent. It is fairly fast to milling and washing, especially when dyed on chromed wool



or when chromed after dyeing, and not sensitive to acids. The levelling properties are moderately good.

**ANTHRAQUINONE BLUE SR (B.A.S.F.).**

Sulphonic acid of di-*p*-tolylamino dibromo diamino anthraquinone produced by condensation of the tetrabromo diamino anthraquinone with *p* toluidine and sulphonation of the product.

Dark blue paste or bluish-grey powder; aqueous solution, bluish-green; HCl, bluer; NaOH, bluer; solution in H<sub>2</sub>SO<sub>4</sub>, red-violet; on diluting, bluish-green.

*Application.*—Anthraquinone blue dyes wool in bright greenish-blue shades with a fine greenish bloom when seen overhand, also in artificial light. It dyes well in an acid bath with the addition of sulphuric acid and Glauber-salt or on chromed wool. But it finds its principal application by the after-chroming method, being dyed with the addition of acetic acid and subsequently chromed with bichromate, although the shades are duller than those which are dyed direct. The fastness to light is excellent, and the colours fixed with chrome are also very fast to washing and milling; the fastness to acids and stoving is good.

**ANTHRAQUINONE GREEN G X (B.A.S.F.).**

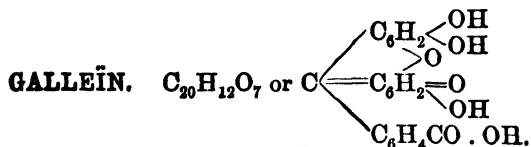
Sulphonic acid of mono- and di-*p* tolylamino *m* sulphanilido anthraquinone produced by condensation of a mixture of mono- and di-chloro *m* sulphanilido anthraquinone sulphonic acid and *p* toluidine.

Bluish-green powder; aqueous solution, green; HCl, green precipitate; NaOH, green precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, indigo blue; on diluting, green precipitate.

*Application.*—Anthraquinone green is dyed principally on wool and less frequently on silk. It is dyed either direct in an acid bath or by the after-chroming method or on chromed material, and produces a bright green of excellent fastness to light, good to acids and alkalies, and fairly fast to washing. The fastness to washing and milling of the colour dyed in combination with chrome is good. The levelling properties are moderately good.

**ANTHRAQUINONE GREEN G X N (B.A.S.F.)** is a new brand, better soluble and brighter in shade than the preceding G X brand. It also levels better, and in other respects it resembles Anthraquinone green G X.

DERIVATIVES OF PYROGALLOL.



**ANTHRACENE VIOLET. ALIZARIN VIOLET.**

Gallein is produced by heating phthalic anhydride with gallic acid to 200°. The gallic acid is thus resolved into carbon dioxide (which escapes) and pyrogallol; the latter forms with phthalic anhydride pyrogallolphthalein or gallein.

Gallein loses one equivalent of water by the action of concentrated sulphuric acid at 200°, and is thereby transformed into Coerulein. Gallein is sold as a violet paste, containing 20 per cent. of dry colouring matter, or as a violet powder. The pure substance, which can be obtained from the dark red alcoholic solution, forms a green crystalline powder with a green reflex.

Gallein is sparingly soluble in boiling water, and forms a red solution; it dissolves in caustic soda with a violet-blue colour, which is turned orange by hydrochloric acid with formation of a dark yellow precipitate. The solution in sulphuric acid is dark yellow, and yields on diluting a finely-divided precipitate, without changing its colour. Gallein forms with the alkalis and alkaline earths, red-violet, and blue soluble compounds; with the oxides of aluminium, chromium, and iron, red to blue-violet insoluble colour lakes. Gallein is reduced by alkaline reducing agents, and forms the leuco-compound gallin,  $C_{20}H_{14}O_7$ .

*Application.*—Gallein is used for dyeing and printing the various fibres; it is always fixed with the aid of mordants, chromium mordants being almost exclusively used. It dyes evenly and combines well with the Alizarins, but its high price, combined with its inferior fastness to light, prevents its extensive application as a colouring matter.

**Cotton** is mordanted with alumina or chromium oxide, or ferric oxide, and dyed in the way described on p. 565. Gallein yields reddish-violet shades on aluminium and on chromium; a dark violet shade on iron mordants. The colour when dyed with chromic oxide is fairly fast to soaping, but is not much faster to light than Methyl violet.

**Wool.**—Gallein is dyed on wool mordanted with bichromate. The methods of dyeing are described on p. 567. Gallein powder is used in the same way as Anthracene brown powder.

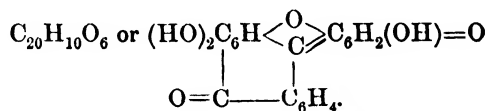
A full violet is produced which is only moderately fast to light and not entirely fast to milling. When dyed on an aluminium mordant the colour is slightly redder and less fast than on chrome mordant; on tin mordant a moderately fast violet-red is produced.

**Silk.**—Gallein can be dyed on silk with the aid of aluminium and chromium mordants; for a full shade about 40 per cent. of paste is required. (See p. 570.)

#### COERULEIN and COERULEIN S.

##### ANTHRACENE GREEN. ALIZARIN GREEN.

Coerulein is probably a derivative of Alizarin, but has not been obtained from it yet. It is prepared by heating Gallein with twenty times its weight of concentrated sulphuric acid to  $200^\circ$ . The constitution is expressed by the formula:



Coerulein, like Alizarin blue, is sold both in the free state and under the name Coerulein S as a bisulphite-compound,  $C_{20}H_{10}O_6 + 2NaHSO_3$ .

Commercial Coerulein is a black paste (containing 20 per cent. of colour), insoluble in water. It dissolves in caustic soda with a green colour; hydrochloric acid produces in this solution a dark precipitate. Concentrated sulphuric acid dissolves Coerulein with a dirty olive-yellow colour; the solution gives a dark green precipitate when diluted with water.

Coerulein yields, on being gently heated with ammonia and zinc dust, a brown-red solution, which contains coerulein,  $C_{20}H_{12}O_6$ , the leuco-compound of Coerulein. This solution is oxidised by the air, and the original Coerulein is reproduced. The reaction might be used for fixing Coerulein on the fibre, as is the case with vat-indigo or Alizarin blue; but the shade is without lustre. Another method of preparing a Coerulein-vat for cotton (which is also applicable for Alizarin blue, Galloeyanine, and similar dyestuffs) has been described in the following manner:—10 kgs. (10 lbs.) of Coerulein paste are mixed in an earthenware vessel with 10 kgs. (10 lbs.) of a solution of ammonium

hydrosulphite, which is prepared in the same way as the sodium hydrosulphite solution (p. 198). A "vat" is obtained by stirring well and diluting with 100 litres (10 galls.) of water; the air absorbed in the water to be used for diluting is rendered innocuous by adding  $\frac{1}{2}$  litre ( $\frac{1}{2}$  pint) of the hydrosulphite solution. The vat is heated with a steam coil to 50° or 60°, and the cotton worked in it for ten to fifteen minutes, and then exposed to the air (*Bull. de Rouen*).

Another method, of theoretical interest, has been proposed by Hunzinger. This method (which also fixes the colour without a mordant) resembles Schlieper and Baum's process of printing with indigo. Calico is prepared with glucose, and printed on with a suitably thickened mixture of Coerulein and caustic soda; the material is run through a rapid ager in order to reduce the Coerulein to coerulein; the latter penetrates the fibre, and is afterwards—by ageing in the atmosphere—reconverted into Coerulein.

Coerulein S is sold both as a black powder and as a black paste (20 per cent.) The powder is about four times as strong as the paste. Coerulein S dissolves in water with a dull green colour. Caustic soda produces in this solution a green flocculent precipitate which is somewhat soluble; hydrochloric acid precipitates from the aqueous solution dark flakes; on heating, sulphurous acid is driven off. Concentrated sulphuric acid gives a dark brown solution, which yields a black precipitate when diluted with water.

COERULEIN B R (M.L.B.) is a paste product which is specially valuable for dyeing wool by the after-chroming method. It resembles ordinary Coerulein in shade and fastness.

*Application.*—Coerulein is used in dyeing cotton, wool, and silk, and especially in calico-printing; it chiefly serves for the production of mixed shades and mode colours. Coerulein, like Alizarin blue, is not a polygenetic colour, and gives with the various mordants similar green shades of an olive or myrtle tone.

Coerulein combines more readily with sodium bisulphite than Alizarin blue, and can be applied similarly to Coerulein S if it is mixed in the dye-bath with the necessary amount of bisulphite. It is even said to give faster colours in this way.

In dyeing with Coerulein, the water must be acidified with acetic acid to prevent loss by the formation of insoluble lime-lakes.

Coerulein does not combine well with Alizarin orange as the latter requires calcareous water; for the shading of Coerulein, Anthracene brown works better than Alizarin orange.

The following remarks apply only to Coerulein S; but Coerulein can be used in the same way after being treated for three days with one-third of its weight of bisulphite of soda.

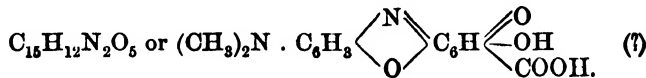
*Cotton.*—Coerulein can be dyed on aluminium mordant by the new red process (p. 565); the mordanted cotton, however, should not be worked in a chalk bath before dyeing; phosphate or silicate of soda or similar fixing agents should be used. For dyeing, water free from lime must be used, and the dye-bath should have 20 c.c. (1 gall.) of neutralised Turkey-red oil per litre (50 galls.) added to it. A fast medium shade of green is obtained. Iron yields a dark olive-green. The mordant almost exclusively used for the fixing of Coerulein is chromium; and the dyeing is effected in the usual way (p. 566). Very fast and dull olive-green shades are obtained with chromium mordants, which equal the best Alizarin colours in fastness. The single-bath method is applicable. (See *Alizarin blues S*.)

*Wool.*—Coerulein is dyed on wool with chromium mordants only, which give excellent results; the fullest shades are obtained if bichromate and tartar, lactic, or formic acid, &c., are used in mordanting, or if the wool is first

mordanted with bichromate and sulphuric acid, and subsequently passed through a bisulphite solution. For methods of dyeing see p. 568. Coerulein BR is suitable for dyeing by the single-bath method. The wool is dyed for one hour at the boil with the addition of Coerulein BR, 4 per cent. sulphuric acid, and 10 per cent. Glaubersalt, 3 per cent. bichromate is then added and the boiling continued for one hour. Coerulein yields from pale sage-green to very dark green shades, which are extremely fast to light, milling, &c.

Silk (see p. 570).—About 25 per cent. of Coerulein S (paste) is required for a full shade with a chromium mordant; aluminium mordants can also be employed.

**GALLOCYANINE** or **FAST VIOLET DH** (Durand and others).



Gallocyanine is produced by the action of nitrosodimethylaniline hydrochloride on gallic acid and belongs to the oxazine-compounds. It possesses by virtue of its chemical constitution both basic and acid properties; the salts which it forms with mineral acids are red, those with metallic oxides are blue-violet. The alkali salts are soluble; those with the alkaline earths and heavy metals are insoluble or sparingly soluble. Alkaline reducing agents convert Gallocyanine into a leuco-compound, from which the original colouring matter is regenerated when exposed to atmospheric oxygen. Gallocyanine is sold as a greenish-grey paste, insoluble in water; it dissolves in caustic soda with a deep violet colour, which becomes crimson on addition of hydrochloric acid; the paste dissolves also in hydrochloric acid to some extent with a light crimson colour. The solution in sulphuric acid is blue and becomes crimson on diluting with water.

**GALLOCYANINE BS** or **FAST VIOLET BS** is the compound of Gallocyanine and bisulphite. It can be prepared by mixing 1 kg. (10 lbs.) of Gallocyanine with 15 to 30 c.c. (1 to 2 pints) of sodium bisulphite (75° Tw.), the mixture being allowed to stand until the dyestuff is dissolved. Its blue aqueous solution is used in dyeing, but should not be exposed for a prolonged period to the air.

*Application.*—Gallocyanine is always fixed with chromium mordants. Its fine blue-violet shade is valuable as a self-colour, and in combination with the wood-colours, Alizarins, and other dyestuffs which dye on chromium mordants, it is suitable for the production of an endless variety of shades.

Cotton is mordanted with alkaline chromium mordant, or the chromium zincate mordant (p. 253), or by any other of the indicated methods. The dyeing with Gallocyanine is started with a fresh cold bath, which is gradually heated to the boil, and kept boiling for one hour.

Gallocyanine yields a bright blue-violet shade, which resists light, soap, and acids well, but is not fast to soda. For a full shade 7 to 8 per cent. of Gallocyanine (of a paste of 20 per cent strength) is required. The colour can be turned to indigo blue by adding Persian berries extract, fustic, or quercitron, or 0.1 to 0.2 per cent. of Methylene blue, and 1 to 2 per cent. of tannin to the dye-bath; in the last case, Gallocyanine acts as a mordant towards Methylene blue, and fixes this dyestuff. By combination of Gallocyanine with Alizarin, Coerulein, &c., a great variety of shades is produced.

The dyestuff can also be fixed with the aid of tannin and antimony in the same way as the basic colours; but this method does not offer particular advantages.

Wool is mordanted with bichromate; the best results are obtained by mordanting with bichromate and an assistant, which reduces the chromic acid entirely.

Enter cold, heat slowly to the boil, and boil for some time. 10 per cent. of Gallocyanine give a full shade; the addition of calcium acetate to the dye-bath is beneficial. The pure blue-violet shade although inferior to Alizarin blue, may be considered very fast to light and to milling. By combination with other mordant colours compound shades are easily produced.

Gallocyanine is largely used in combination with logwood.

Aluminium, iron, copper, and tin mordants produce similar shades with Gallocyanine as chromium mordants, which, however, do not possess the same brilliancy and permanence.

Silk is dyed according to the general methods indicated on p. 570.

A great number of dyestuffs, closely related to Gallocyanine, both by their chemical constitution and their tinctorial properties, have been prepared, especially so by L. Durand, Huguenin & Co., which firm first manufactured the Gallocyanine. Some of the most important products of this kind will be described in the following pages, especially those used in dyeing, whereas the majority of these colours are chiefly valuable for calico-printing.

#### **GALLANILIC VIOLET BS (Durand).**

Gallanilic violet BS is the bisulphite-compound of *Gallanilic violet*, which is produced by the action of gallanilide on nitrosodimethylaniline. It forms an olive-green paste, which is insoluble in water, and dissolves in caustic soda with an intense violet colour. Hydrochloric acid turns this solution reddish-violet and produces a reddish-violet precipitate. The solution in concentrated sulphuric acid is reddish-violet and gives a reddish-violet precipitate on diluting with water.

*Application.*—Same as Gallocyanine; the shade is nearly the same.

#### **GALLANILIDE BLUE (Durand).**

Gallanilide blue is produced by the action of gallanilide on nitrosodimethylaniline and subsequent treatment with aniline. Its sulphonic acid is an acid colour known as Gallanilic indigo P S. Both colouring matters are phenylated derivatives of Gallanilic violet.

Gallanilide blue is similar to Gallocyanine, and is applied in the same way. It dyes a somewhat bluer shade.

#### **DELPHIN BLUE (Kern). CRUMPSALL FAST BLUE (Levinstein).**

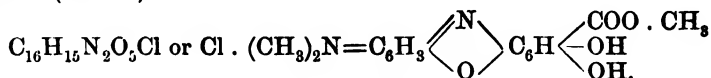
Delphin blue is the sulphonic acid of a product obtained by heating Gallocyanine with aniline. The commercial product is sold either as a dark paste (in the form of the free sulphonic acid) or as a dark brown powder (in the form of the ammonium salt). The latter dissolves in water with an intense violet colour. The dyestuff is precipitated from this solution by hydrochloric acid, while caustic soda gives a soluble reddish precipitate. The solution in sulphuric acid is red-violet and does not change in appearance on diluting.

*Application.*—Delphin blue is dyed on metallic mordants, chiefly on chrome, and is specially adapted for wool dyeing. It gives greenish-blue shades on cotton and may be dyed on this fibre in the same way as Gallocyanine. It dyes on wool and silk bluer shades than those obtained with Gallocyanine or Alizarin blue. The single-bath method does not yield fast shades on wool; but such are obtained by saddening with salts of copper or iron. It is best to dye on chromed wool according to the method stated (p. 568). Bichromate with tartar, lactic, or formic acid, is the best mordant; with sulphuric acid as an assistant less bright colours are obtained. A blue, fairly fast to light and fast to milling, is produced on a pure chrome

mordant which, spotted with nitric acid, yields a test similar to that of indigo. Mordanting with bichromate, copper sulphate, and tartar or sulphuric acid produces colours which are very fast to light and milling, though not very bright. Aluminium gives redder shades, which are not very fast.

Delphin blue or Crumpsall fast blue when dyed on unmordanted wool produces violet colours, which are not fast to soap or light.

**PRUNE** (Sandoz).



Prune is the methyl-ether of Gallocyanine, and is produced by the reaction of nitrosodimethylaniline hydrochloride with the methyl-ether of gallic acid.

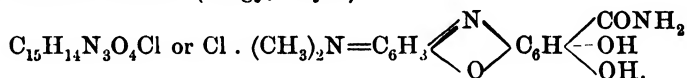
Prune forms brown glittering crystals, or a dark brown powder, and is readily soluble in water with a red-violet colour. The aqueous solution becomes crimson on addition of hydrochloric acid, and yields with caustic soda a soluble violet precipitate. The solution in sulphuric acid is blue, and becomes crimson on diluting with water.

*Application.*—Prune is chiefly used in calico-printing and is fixed with the aid of metallic mordants; it can also be printed with tannin.

Cotton is dyed, as with the basic colours (on a mordant of tannin and antimony, or it is mordanted with an aluminium salt and dyed in a very slightly alkaline bath with Prune. Prune dyes plum shades, which are fairly fast to soap and light.

Wool and silk can be dyed with Prune by the general methods (pp. 568 and 570) on chrome mordants. The colour is suitable for combinations with other mordant colours and equals Delphine blue in fastness.

**GALLAMINE BLUE** (Geigy, Bayer).



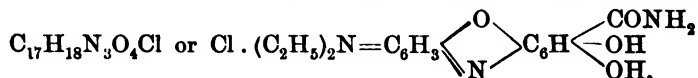
Gallamine blue is produced by a modification of the process for preparing Gallocyanine, gallamic acid ( $C_6H_2(OH)_3CONH_2$ ) being used instead of gallic acid.

The commercial product is a dirty green paste, slightly soluble in boiling water with a green colour; it dissolves more readily in hydrochloric acid with a red colour and in caustic soda with a violet colour. The solution in sulphuric acid is red and in thin layers green, and remains red on diluting with water.

The colour is also sold in the form of a soluble bisulphite compound.

*Application.*—Gallamine blue is recommended for the production of compound shades in calico-printing and wool dyeing. It produces on wool which has been mordanted with bichromate of potash and tartar a blue-violet similar to Gallocyanine, which, however, is partly discharged by soap or acid, and is but moderately fast to light.

**COREINE R R** (Durand). **CELESTINE BLUE B** (Bayer).



This dyestuff is produced by the action of nitrosodiethylaniline or diethylaminoazobenzene upon gallamic acid.

Greenish-black powder (Celestine blue) or thin brown paste (Coreine); aqueous solution, violet-blue; HCl, magenta-red solution and soluble precipi

tate; NaOH, blue solution and soluble violet precipitate; solution in  $H_2SO_4$ , blue; on diluting, magenta-red.

*Application.*—Coreine or Celestine blue, in combination with chrome mordants, dyes a bright reddish-blue, and is well adapted for wool dyeing and calico-printing, but not very suitable for cotton dyeing. Wool is best mordanted with chromium fluoride and oxalic acid, or with bichromate and an effective reducing assistant, and dyed (one to one and a-half hour's boiling) with the addition of acetic acid. A bright blue-violet is obtained which is fairly fast to light, acids, and alkalies, and fast to milling, similar to Delphine blue. On bichromate the colour is not quite as bright as on fluorochrome. Silk may be dyed according to the general methods indicated on p. 570.

#### COREINE A R and A B (Durand).

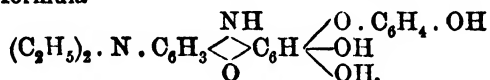
These two brands are produced by the action of aniline and subsequent sulphonation on the products of condensation of dialkylaminoazobenzene on gallamic acid (like Coreine R R).

Black paste; aqueous solution, blue; HCl, brown precipitate (A B) or violet-brown precipitate, soluble with a red-violet colour (A R); NaOH, redder solution; solution in  $H_2SO_4$ , blue-violet; on diluting, magenta-red.

*Application.*—Coreine A R and A B are dyed on chrome-mordanted wool or cotton, and are also used in calico-printing. They dye greenish shades of blue, which are very fast to washing and milling, acids, and alkalies, and fairly fast to light; the shade of Coreine A B is slightly more greenish than that of A R.

#### PHENOCYANINE V S, T C, T V (Durand).

Phenocyanine V S is produced by the action of resorcin upon the Gallo-cyanine from diethylaniline and gallic acid. Its chemical constitution is expressed by the formula—



It is a leuco-compound, the alkaline solution of which rapidly becomes blue in the air. The brand T V is obtained by sulphonating V S by heating with sulphites and T C by oxidising V S.

*Phenocyanine V S.*—Greenish-yellow paste or greenish solution; HCl, soluble green precipitate, with excess of HCl, dirty grey solution; NaOH, brown solution rapidly becoming blue in the air; solution in  $H_2SO_4$ , brown, and gradually becoming blue in the air.

*Application.*—The Phenocyanines are used in combination with chrome mordants in wool dyeing, and principally in calico-printing. They dye indigo shades of very good fastness to light, washing, milling, acids, and alkalies. Duller shades of good fastness are obtained by the after-chroming method.

#### CHROMOCYANINE V and B (Durand). BLUE P R C (Durand). BRILLIANT GALLOCYANINE (Durand).

These dyestuffs are sulphonic acids of leuco-gallocyanines which are produced by the action of sulphite on various gallocyanines.

*Chromocyanine V.*—Dark paste; aqueous solution, violet; HCl, soluble red-violet precipitate; NaOH, redder solution, becoming blue in the air; solution in  $H_2SO_4$ , dark violet; on diluting, red-violet.

*Application and Properties.*—Like Phenocyanine, the Chromocyanines dye bright violet shades, the two other dyestuffs bright blue shades of good fastness.

#### GALLAZINE A (Durand).

Gallazine A is produced by condensation of Gallo-cyanine with beta-naphthol sulphonic acid S and subsequent oxidation.

Black paste ; aqueous solution, blue ; HCl, produces a precipitate, soluble with a red-violet colour ; NaOH, violet solution ; solution in  $H_2SO_4$ , blue ; on diluting, violet and violet precipitate.

*Application.*—Gallazine A is dyed on chrome-mordanted wool and cotton, and chiefly used in calico-printing. It yields indigo-blue shades of fairly good fastness to light, and very good fastness to washing, milling, acids, and alkalies. It may also be dyed on wool, like the acid colours and the acid chrome colours ; when after-treated with bichromate, it yields less bright blues, which, however, are still faster to milling than those on chromed wool.

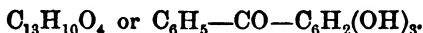
**GALLOFLAVIN (B.A.S.F.).**  $C_{13}H_6O_9$  (?).

Galloflavin is produced by the limited oxidation of gallic acid in an alkaline solution ; the constitution of the compound is not known.

The commercial article forms a dull greenish-yellow paste containing 20 per cent. of colouring matter ; it is insoluble in water, but dissolves in caustic soda with an orange colour, and is precipitated from this solution by hydrochloric acid as a yellowish flocculent mass. Galloflavin dissolves in sulphuric acid with a yellow colour ; the solution yields a yellowish-grey precipitate on diluting. Galloflavin, when dyed on mordanted wool, yields with bichromate mordant an olive-yellow, with copperas a dark brown, with stannous mordant a dull orange, and with copper sulphate a brown shade.

*Application.*—Galloflavin combines well with the Alizarins, and is used in dyeing and printing cotton, wool, and silk ; for fixation, chromium mordants only are used, and shades similar to old fustic are obtained, which are fairly fast to light, soap, and milling, fast to dilute acids and alkalies, but do not compare favourably with the Alizarins. The colour is somewhat sensitive to chlorine. The general methods given in the introduction (pp. 565 to 570) are applicable.

**ALIZARIN YELLOW A (B.A.S.F.).**



Alizarin yellow A or *trioxybenzophenone* is (like the following Alizarin yellow) not a true Alizarin colour. It is produced by condensation of benzoic acid or benzotrichloride with pyrogallol, and is sold as a grey paste, which dissolves in boiling water ; hydrochloric acid has no action on the solution ; caustic soda dissolves the paste, producing an intensely yellow solution which is soon changed by oxidation. The solution in sulphuric acid is yellow ; on diluting, a pale yellow precipitate is obtained.

*Application.*—Alizarin yellow A is used in cotton dyeing, and especially in calico-printing, on aluminium mordant. It produces orange-yellow shades, which are fairly fast to light, soap, and chlorine. The dyestuff is not very well adapted for dyeing proper. The fourth Turkey-red method in its simplified form (p. 591) may be used for dyeing.

**ALIZARIN YELLOW C (B.A.S.F.).**



Alizarin yellow C or *gallacetophenone* is produced by the action of glacial acetic acid and chloride of zinc on pyrogallol.

The commercial article forms a grey paste containing 20 per cent. of dry colouring matter, which dissolves freely in hot, less in cold, water ; hydrochloric acid has no action on the solution ; caustic soda colours it brown, and changes the dyestuff by oxidation. The colouring matter dissolves in sulphuric acid with a yellow colour ; the solution yields a yellowish precipitate on diluting.

*Application.*—Alizarin yellow C is used, like Alizarin yellow A, chiefly for calico-printing with the aid of aluminium mordant. It yields fairly fast



shades. On aluminium, greenish-yellow; on chromium, brown; on iron, slate to black colours are obtained. It is also not very well adapted for dyeing proper. For methods of dyeing, see pp. 565 and 591.

## VARIOUS PHENOLIC COMPOUNDS.

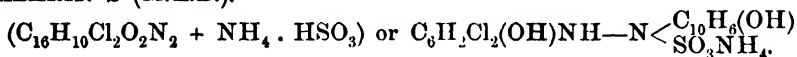
### RESOFLAVIN (B.A.S.F.).

Resoflavin is the product of oxidation of *m* dioxybenzoic acid in sulphuric acid solution by means of ammonium persulphate or by the oxidising action of the electrical current.

Yellow paste or powder, almost insoluble in water; the solution in aqueous caustic soda is red-brown; HCl forms in this solution a yellow precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, yellow with a green fluorescence; on diluting, yellow precipitate.

*Application.*—Resoflavin is dyed on chromed wool, according to p. 568, an olive-yellow of very good fastness to light, milling, washing, alkalies, and acids being produced. It may also be dyed in an acid-bath, and subsequently fixed with chromium fluoride but not with bichromate.

### AZARIN S (M.L.B.).



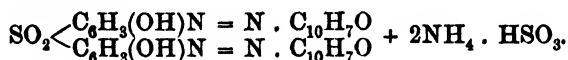
Azarin S is a compound of *dichlorophenolazobetanaphthol* and ammonium bisulphite. The azo-compound is not soluble in water, but it is converted by the action of ammonium bisulphite into a soluble hydrazo-compound, which is dissociated by a high temperature similarly to Alizarin blue S, &c. On this property is based its application in dyeing and printing.

Azarin S comes into commerce as a yellow paste, very similar to Alizarin in appearance, but smelling of sulphur dioxide; it dissolves sparingly in water with a yellow colour; hydrochloric acid produces in this solution an orange-yellow precipitate; caustic soda forms a violet precipitate with a red colour. Sulphuric acid dissolves the dyestuff with a crimson colour; on diluting, the solution yields a red-brown precipitate.

*Application.*—Azarin S is chiefly used for the preparation of beautiful red and pink lakes, which resist light very well. It may also be used for the dyeing of cotton and silk, as also in calico-printing, and can be applied in the same way as Alizarin red; only, it requires, in addition to the aluminium mordant, a stannous compound for fixation. The following process has been recommended for cotton piece goods:—Mordant on the padding machine in a bath containing 10 parts of aluminium acetate (12° Tw.), and 1 part of stannous hydrate paste, age for twelve to twenty-four hours, dung in cow-dung or in a chalk-bath at 55°, wash, and dye; prepare the dye-bath with 3 parts of Azarin (20 per cent.) and 1 part Turkey-red oil, raise the temperature in one hour to 75° or 80°, dry, pass through Turkey-red oil, steam, wash, and soap.

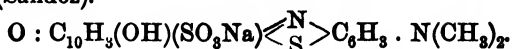
Azarin S dyes a very bright red shade somewhat bluer than Alizarin, which is very fast to soap, but inferior to Alizarin in fastness to light. The high price prevents an extensive employment of the product.

### AZARIN R (M.L.B.).



Azarin R is the azo-compound of diamino-oxysulphobenzide and beta-naphthol, combined with ammonium bisulphite. It resembles Azarin S.

**BRILLIANT ALIZARIN BLUE G and R** (Bayer, Claus & Co.). **INDO-CHROMINE T** (Sandoz).



Brilliant Alizarin blue is produced by condensation of nitrosodimethylaniline, nitrosomethyl or ethylbenzylaniline sulphonic acid, &c., on betanaphthoquinone or its sulphonic acid in the presence of sodium thiosulphate, and its constitution is indicated by the above formula.

*Brilliant Alizarin Blue G.*—Greenish-brown, bronzy paste, or bronzy-brown powder, soluble in hot water, crystallising on cooling; solution in aqueous caustic soda, violet-blue; HCl, produces in the alkaline solution a violet precipitate; solution in  $H_2SO_4$ , green; on diluting, violet precipitate.

*Brilliant Alizarin Blue R.*—Violet-black paste or dark brown powder; aqueous solution, blue-violet; HCl, blue precipitate; NaOH, blue-black precipitate, soluble with a greenish-blue colour; solution in  $H_2SO_4$ , olive-green; on diluting, at first blue, then green.

*Application.*—Brilliant alizarin blue is used in combination with chrome mordants for wool and silk dyeing, and for calico-printing, and yields very pure shades of blue, which are very fast to light and other influences. Water containing much calcium bicarbonate may be softened by boiling with sodium sulphate.

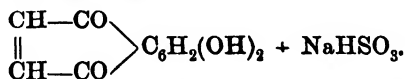
*Wool.*—Brilliant alizarin blue requires a weak chrome mordant, 2 to 2½ per cent. bichromate, with tartar, lactic acid, &c., but for pale shades still weaker mordants are preferable. The dyestuff is best dyed in a boiling bath in order to prevent it from crystallising. Boil the dye-liquor for five minutes with the addition of 10 to 20 per cent. Glaubersalt, add the well-dissolved dyestuff through a sieve, enter the material into the boiling liquor, add, after fifteen to twenty minutes, 2 per cent. acetic acid (in one or two portions), boil all together one and a-half to two hours, rinse, and dry. Brilliant alizarin blue may also be dyed without previous mordanting with the addition of acetic acid and Glaubersalt, and subsequently be fixed with chromium fluoride, but not with bichromate. It yields in both ways very fine blue shades fast to milling, washing, acids, and alkalies, and of excellent fastness to light in full or pale shades. The "G" brand yields a bright greenish-blue, the "R" brand a redder blue. By dyeing in an acid-bath, and subsequent treatment with 1½ per cent. stannous chloride and 1 per cent. sulphuric acid, much brighter colours of equal fastness to light, but inferior fastness to milling, are obtained.

Silk is dyed, after previous chroming (p. 570), the colours being very fast to light, soap, water, acids, and alkalies.

**BRILLIANT ALIZARIN BLUE S D** is a brand intended for calico-printing.

**BRILLIANT ALIZARIN BLUE 3 R** is a recent brand, resembling "It" in reactions and properties, but more reddish in shade, and dyes more level.

**ALIZARIN BLACK, R, W R, S or S R** (B.A.S.F. and others).



Alizarin black is *dioxynaphthoquinone* or *naphthazarin*. It is produced by the action of zinc and concentrated sulphuric acid on alpha-dinitronaphthalene, and subsequent treatment of the quinone thus obtained with sodium bisulphite.

Alizarin black R and the more concentrated and purer brand W R are black-brown pastes, difficultly soluble in water; the solution in caustic soda-lye is blue, and is precipitated by hydrochloric acid; solution in  $H_2SO_4$ , red; on

diluting, brown precipitate. Alizarin black R is also furnished to the trade as a black powder, six times as strong as the paste.

Alizarin black S or S R forms a black paste smelling of sulphur dioxide, or a black powder, five times as strong, and is soluble in cold water with a red-brown colour; hydrochloric acid has no action on the solution, caustic soda turns it blue. The solution in sulphuric acid is dark olive, and becomes red on heating, evolving the smell of sulphur dioxide; the olive solution yields a dark brown precipitate on diluting.

The bisulphite compound is stable towards the action of hydrochloric acid or diluted sulphuric acid; by ammonia, caustic alkalies, and alkaline carbonates it is resolved into the two components. The same decomposition takes place in dyeing; dioxynaphthoquinone is liberated on heating, and combines with chromium hydroxide to form the colour-lake.

*Application.*—Alizarin black is principally used in calico-printing and in wool dyeing for the production of fast black shades with the aid of chromium mordants; but it is not extensively employed in cotton dyeing, since it is difficult to obtain full shades, and the colouring matter is too expensive.

Cotton is mordanted with H. Koechlin's alkaline chromium mordant (p. 251), and dyed in a concentrated bath, with the addition of acetic acid (3 parts for 1,000 parts of dye-liquor) and common salt (25 per cent. of the weight of the material); 40 per cent. Alizarin black S are required for a full shade. A reddish-black is obtained which is extremely fast to all agents; a jet-black may be produced by shading with Coerulein or other mordant colours. Alizarin black may be dyed exactly like Alizarin blue S by the single bath or padding method (p. 609).

Wool is mordanted with bichromate, and dyed by the methods given on p. 568. 3 per cent. of Alizarin black S in paste is required for a slate shade, and 20 to 35 per cent. for a full black (which appears slightly reddish). The colour combines well with other mordant dyestuffs, and is exceedingly fast to light, milling, rubbing, acids, and alkalies.

Alizarin black W R may be employed with advantage for the production of full shades in *one* bath. The bath is prepared with 1 to 3 litres (galls.) acetic acid, 30 per cent. for 1,000 litres (galls.) water, and, after entering the wool, it is heated within half an hour to the boil, and boiled one hour; it is then cooled off to 80° C. (for loose wool cooling may be dispensed with), and 1½ per cent. bichromate is added; finally, the colour is developed and fixed by one hour's boiling. This black possesses the same fastness as that produced in two baths, except that it tends to rubbing.

The makers of Alizarin black formerly recommended the following process:—Prepare the bath at a temperature not exceeding 50° C. with 6 kgs. (lbs.) chromium acetate, 32° Tw., for 100 kgs. (lbs.) of wool; enter the material, and boil for one hour, cool with cold water to 70°, add the required amount of dyestuff gradually, and boil one hour more. After this time add, to develop the shade completely, 3 to 4 kgs. (lbs.) liquor ammonia for every 100 kgs. (lbs.) of material, and boil again for half an hour; finally, rinse well.

Another process of dyeing Alizarin black by the one-bath method, which was also proposed by the makers, consists in boiling unmordanted wool with 35 per cent. of Alizarin black in a concentrated bath for one hour, adding a solution of 10 per cent. of alum, 1 per cent. of copper sulphate, and ½ per cent. of oxalic acid to the bath, and boiling one and a-half hours longer. The black will be bluer if, after this time, 1 to 1½ parts of ammonia are added to the dye-bath for every 1,000 parts of liquor, and the boiling is continued for half an hour. While adding the ammonia the wool has to be taken out.

Silk is mordanted previous to dyeing with chromium by the methods given on p. 570.

Alizarin black can also be dyed on silk without boiled-off liquor; in this case a concentrated bath is required containing 7 parts of Alizarin black paste in 100 parts of water. Enter cold, heat gradually in the space of forty-five minutes to the boil, and boil for one hour longer; wring and rinse well; soap for fifteen minutes in boiling soap solution, 2 grms. per litre ( $\frac{1}{3}$  oz. per gall.), brighten with acetic acid, wring, and dry.

An iron mordant is also recommended by the makers for dyeing Alizarin black on silk in the following manner:—Work the silk for two hours in a bath of stannic chloride (52° Tw.), wring and rinse well, and soap for two hours at 35° C. with 5 per cent. soap and 60 per cent. soda crystals. Then work the silk for half an hour in nitrate of iron (52° Tw.), rinse, soap for one and a-half hours at 75° C. in a 10 per cent. solution of neutral soap, and rinse again. After this, work the silk in a bath of 10 per cent. yellow prussiate of potash and 20 per cent. hydrochloric acid (which treatment imparts a bluish tone, see p. 271), and steep for two hours at incipient boiling in a solution of 50 per cent. catechu (of the weight of the silk); rinse again. Dye with 30 per cent. Alizarin black W R in a bath containing 5 per cent. neutral soap and a small amount of acetic acid; enter cold, heat in one hour to the boil, and continue boiling for one and a-half hours. For lighter weighting the treatment with stannic chloride and the following soaping may be omitted.

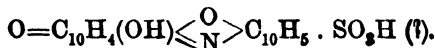
#### ALIZARIN DARK GREEN W (B.A.S.F.).

Alizarin dark green W is produced by a treatment of the naphthazarine melt (see *Alizarin black*, p. 625) with phenols.

Black paste or powder, difficultly soluble in water; solution in caustic soda-lye, blue; on addition of HCl, dark violet precipitate; solution in  $\text{H}_2\text{SO}_4$ , dark violet; on diluting, redder and dark precipitate.

*Application.*—Alizarin dark green W is dyed either on chromed wool or in an acid bath with subsequent chroming with bichromate, or with chromium fluoride. On chromed wool, if subsequently chromed with fluorochrome, it dyes dark bluish-green shades, and if chromed with bichromate, dark yellowish-green shades of fairly good fastness to light and milling, and good fastness to acids and alkalis. It is useful for shading and saddening colours on piece goods, and is best dyed in an acid bath, and subsequently chromed with bichromate.

#### ALIZARIN GREEN B and G (Dahl).



These two dyestuffs belong to the oxazine group and are produced by the action of beta-naphthoquinone sulphonic acid on (2) amino- (1) naphthol- (4) sulphonic acid ("B" brand) or on (1) amino- (2) naphthol- (6) sulphonic acid ("G" brand).

Dark bluish-green (B) or black (G) powder, difficultly soluble in water; aqueous solution, bluish; HCl, dark precipitate, soluble with a violet colour (B) or crystalline precipitate, readily soluble with a red colour (G); NaOH, soluble green precipitate; solution in  $\text{H}_2\text{SO}_4$ , pale dark blue (B) or pale blue-green (G); on diluting, violet.

*Application.*—Alizarin green B and G are dyed on chromed wool in a bath feebly acidulated with acetic acid exactly like the Alizarins (p. 568). Enter lukewarm, heat within one hour to 70° C. and then to boiling, boiling one to one and a-half hours; in order to make the shade more bluish and faster to alkaline milling, cool the bath, add 1 part ammonia liquor for 1,000 parts of dye-liquor and work five to ten minutes without steam. Fairly bright

green shades of good fastness to milling, acids, and alkalies, and fairly good fastness to light are obtained in this way. They become red-brown by carbonising, but the original shade is restored by ammonia.

On chromed silk, green shades fast to water and washing are obtained.

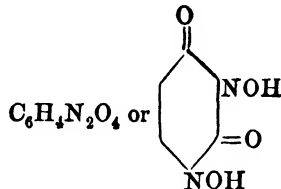
### QUINONEOXIMES OR NITROSO-COMPOUNDS.

By the action of nitrous acid on certain phenols compounds are obtained which are frequently called nitroso-phenols, the correct name of which, however, is "quinoneoxime," since they do not contain the nitroso-group NO, but the quinoneoxime-group  $\begin{cases} \text{O} \\ \text{NOH} \end{cases}$ . The orthoquinoneoximes dye on metallic mordants, according to St. v. Kostanecki,\* while the other quinoneoximes do not.

The combination of atoms  $\begin{array}{c} \text{C} \text{---} \text{O} \\ | \quad | \\ \text{C} \text{---} \text{N}(\text{OH}) \end{array}$  acts both as a chromophorous and as an auxochromous group. These colours are permanently decolourised by the action of reducing agents, aminophenols being formed.

The nitroso-compounds are used almost exclusively in combination with iron mordants in calico-printing, and invariably produce with this metal green shades, which are distinguished by fastness to light. Cobalt or nickel mordants yield rich browns. Naphthol green B (Cassella), an acid dyestuff (p. 555), also belongs to this group.

#### DINITROSO-RESORCIN.



#### CHLORIN. FAST GREEN. DARK GREEN. RUSSIAN GREEN. ALSACE GREEN.

Dinitroso-resorcin forms a grey powder, sparingly soluble in cold, but more soluble in hot water. It forms two classes of salts; the acid salts with one equivalent of alkali are crystalline and sparingly soluble in water; the neutral salts with two equivalents of alkali are readily soluble in water. The ferric salt is dark green.

The commercial product is sold as a dark grey paste (the dry powder being explosive), which dissolves in water with an olive-yellow colour. Hydrochloric acid has no action on the solution; caustic soda makes it darker. The solution in sulphuric acid is pale yellow, and becomes lighter on being diluted with water.

*Application.*—Dinitroso-resorcin may be used in dyeing cotton piece goods. The material is mordanted with pyrolignite by padding, ageing, and fixing with silicate of soda and chalk; then, after being washed in water, it is dyed in a neutral bath or in one which has been very slightly acidified with acetic acid (to neutralise lime), entered at the ordinary temperature, heated in forty-five minutes to the boil, washed, and dried. Dinitroso-resorcin dyes a dark olive-green, fairly fast to light and moderately fast to soap.

\* *Journ. Soc. Dyers and Col.*, 1888, p. 7.

H. Koechlin has produced on calico a fine brown with the aid of a cobalt mordant by printing a paste prepared with 29 grms. of cobalt nitrate, 25 grms. of sodium acetate, and 1 litre of tragacanth size, passing through aluminate of soda at 30° C. and dyeing in a bath containing 5 grms. of Dinitroso-resorcin and 6 grms. of a solution of calcium chloride (32° Tw.) per metre of calico. Nickel salts may also be used in place of cobalt salts.

Very fast green and brown colours can be produced on wool or silk by similar processes. Wool is mordanted with 10 per cent. copperas with the addition of 5 to 10 per cent. tartar or oxalic acid, well rinsed, and dyed with very gradual heating in a feebly acid-bath. On chromed wool a tobacco brown is produced. Silk is mordanted in nitrate of iron and slowly dyed in a feebly acid bath.

### ESSAÏN.

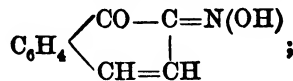
Essaïn is a brown colouring matter obtained from Dinitroso-resorcin. According to H. Schäffer\* and F. Binder,\* for the production of Essaïn 350 grms. Dinitroso-resorcin paste (50 per cent.), 255 c.c. hydrosulphite of sodium, and 312 c.c. water are mixed. The hydrosulphite is prepared by reducing 700 c.c. of sodium bisulphite (82° Tw.) with 200 grms. of zinc dust. At first the reaction is slow, but it soon becomes more active, and a considerable amount of froth is formed; the reaction lasts about two hours and a-half (during which time the mixture must be stirred to regulate the action of the reducing agent) and the temperature rises to 58°. After cooling, the colouring matter is filtered, and is obtained as a perfectly clear brownish-red liquid which mixes in any proportion with water or acetic acid.

*Application.*—Essaïn has been used for some time in the United States for calico-printing. It can also serve for wool printing and wool dyeing. It produces pure reddish-brown shades, fast to soap, acids, and alkalis, but especially to light. It is fixed by means of chromium mordants. Wool is mordanted with bichromate and dyed in a fresh bath with Essaïn with the addition of some oxalic acid (*Schäffer*). About 8 per cent. of the colouring matter produces an average brown.

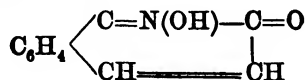
### NITROSO-NAPHTHOL. $C_{10}H_7NO$ .

GAMBIN R and Y (Holliday, Berlin). ALSACE GREEN J (Thann).

Two isomeric compounds of very similar properties are in the market which are produced by the action of nitrous acid on alpha-naphthol and beta-naphthol respectively. Both are *naphthoquinoneoximes*. Nitroso-alpha-naphthol (Gambin R), the product of alpha-naphthol, is



nitroso-beta-naphthol (Gambin Y) is



They form greenish-brown pastes, sparingly soluble in water. The aqueous solution is not affected by hydrochloric acid; in caustic soda the colours dissolve freely with a yellow colour. The solutions in sulphuric acid are brown and yield brown precipitates on diluting with water.

*Application.*—The Nitroso-naphthols are principally used in calico-printing and in wool dyeing. They produce with iron mordants olive-greens, approaching the shades obtained by Dinitroso-resorcin; with chromium

\* *Journ. Soc. Dyers and Col.*, 1891, p. 138.

mordants, catch shades; with nickel salts they produce bronzes; with cobalt, catch-browns; with cerium bronzes with a brown tinge; with uranium, yellows. The shades obtained by Nitroso-alphanaphthol are in general darker than those obtained by Nitroso-betanaphthol.\* The Nitroso-naphthols may be used for dyeing cotton or wool, producing with the usual mordants shades which are very fast to light and soap. For printing, their application is more difficult, because they appear to be volatilised and, perhaps, to decompose on steaming.

The colour should be well mixed with three or four times its weight of cold water before being added to the dye-bath; wooden vessels should be used, as iron in any form tends to green the shades produced.

Cotton is dyed by exactly the same method as with Dinitroso-resorcin.

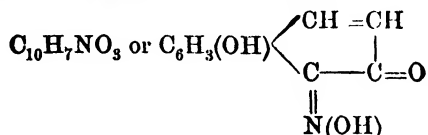
Wool.—*Browns* are produced by previously mordanting the wool with potassium bichromate with, or without, the addition of tartar or sulphuric acid; the latter makes the shade redder. For a full shade, up to 30 per cent. of Nitroso-naphthol is required. Add the colour to the lukewarm bath, enter the goods, heat slowly to the boil and boil for half an hour or more.

*Olive* shades are obtained by proceeding in the above manner and then saddening to the required shade with ferrous sulphate; the longer the material remains in this bath and the more copperas there is used, the greener is the shade.

*Green*.—Mordant with 3 per cent. of ferrous sulphate and 1 to 3 per cent. of tartar, wash and dye in a fresh bath with Nitroso-naphthol in the same manner as for brown; if the wool is afterwards boiled with bichromate the shade can be turned to an olive.

The Nitroso-naphthols combine well with wood-colours, Alizarins, and other mordant-colours. The colours on iron mordants are extremely fast to light those on chromium mordants not quite so, although very fast in full shades.

DIOXIN (Leonhardt). GAMBIN B (Holliday).



Dioxin is the product of the reaction of nitrous acid on (2:7) dioxy-naphthalene. It forms a brown paste, which is sparingly soluble in water with a brown colour. It dissolves in caustic soda with an intense brown-red colour, and is precipitated from this solution by hydrochloric acid. It dissolves in sulphuric acid with a bright green colour; this solution yields a red-brown precipitate on diluting with water.

*Application*.—Dioxin is dyed on wool either with an iron mordant (copperas and oxalic acid or tartar) or with a chrome mordant by the methods given for Nitroso-naphthol. It yields with iron a yellowish-green which is brightened by milling; with chrome it produces a brown which is not fast to milling, but does not bleed into the white; on wool mordanted with mixtures of chrome and iron compound shades may be produced. The various shades resist the action of light well.

\* Ed. Koechlin, *Journ. Soc. Dyers and Col.*, 1891, p. 137.

## ACID CHROME COLOURS.

This is a comparatively new group of colours, a few of which only were named in the first edition of this book, the method of after-chroming then being hardly known.

The group consists of dyestuffs which can be dyed on wool in an acid bath, and may be after-treated on the fibre by bichromates or chromium salts. The majority of the acid chrome colours are azo-compounds, principally derivatives of salicylic acid or of orthoaminophenol. A number of derivatives of anthracene or of pyrogallol, which by their tinctorial properties might have been classed under this group, have been described under the heading of *Mordant Colours*, while, on the other hand, various other products, such as Chromogen I (M.L.B.)—i.e., 1 : 8 dioxynaphthalene 3 : 6 disulphonic acid, or chromotrop acid—will be considered here. Various triphenylmethane colours—e.g., Patent blue A and Brilliant milling green B—can also be dyed in the same way, and are very useful for shading and brightening.

The dyestuffs of this group are chiefly dyed on wool, and find little application on the other fibres. They are most generally dyed by the after-chroming method; but a great many can also be dyed on chromed wool, and some of them may be dyed direct in an acid bath on wool without any after-treatment. Aluminium salts are rarely used for these colours. On silk the acid chrome colours might be used in the same way as on wool but for the reason that an after-treatment with bichromate is not very suitable for the silk fibre. Some of them are dyed direct on silk owing to their good fastness to water on this fibre. A few members of this group are used in calico-printing in combination with chromium salts.

The majority of the acid chrome colours are distinguished by very good fastness to light, washing, milling, alkalies, acids, perspiration, rubbing, and to wearing in general. Some are also fast to acid cross dyeing, stoving, and potting or wet steaming. The colours belonging to different chemical groups do not show a uniform behaviour; but, as a rule, only such products are recommended for acid chrome dyeing as are very fast to light and milling when dyed in this way. The acid chrome colours may also be dyed direct, but many of them are without value unless fixed with chrome.\*

The acid chrome colours are chiefly used for the production of colours fast to milling—i.e., on loose wool, slubbing, or tops and yarns, but also for colours fast to wearing on piece goods, especially gentlemen's suitings.

**Dyeing of Wool.**—The *after-chroming* or *one-bath method* is carried out in the following way:—The bath is prepared with the necessary colouring matter, 10 per cent. Glaubersalt, and 1 to 5 per cent. acetic acid 30 per cent. (8° Tw.). After entering the material at 40° to 60° C., the bath is heated gradually to boiling, and boiled for about one hour, during which time it is exhausted by the addition of 5 to 8 per cent. acetic acid, or 1 to 4 per cent. sulphuric acid. After slightly cooling off the liquor, the required quantity of bichromate—usually about one-half to two-thirds the weight of dyestuff (in powder)—is added, and the bath boiled again for a-half or three-quarters of an hour. With

\* Many of the acid chrome colours show a totally different colour in combination with chrome to the direct dyed shades, especially when after-chromed—e.g., many of the blacks and blues dye in an acid bath a red or crimson shade which, by after-chroming or dyeing on chromium mordants, are converted into black or blue. Most of such colours are not suitable for direct dyeing. Exceptions are—e.g., the Chromotropes—discussed under the heading of *Acid colours*, which might also be included under the *Acid chrome colours*.



many dyestuffs, instead of acetic acid, 1 to 4 per cent. sulphuric acid (5 per cent. for blacks), or about the same quantity of formic acid (85 per cent.), may be used; an excess of sulphuric acid frequently causes the shade to be dulled by the chroming.

Chromium fluoride is used instead of bichromate with a few dyestuffs which do not resist the oxidising action of chromic acid. It has, however, not found much favour, since the majority of colours are not fixed well, and the liberated hydrofluoric acid gives the wool a harsh feel.

Some dyestuffs—*e.g.*, *Chromate black* (Berlin)—are treated with advantage with a mixture of  $1\frac{1}{2}$  to 2 per cent. bichromate, and  $1\frac{1}{2}$  to 2 per cent. cupric sulphate, to which, for dark shades, 3 per cent. acetic acid, or  $\frac{1}{2}$  to 1 per cent. sulphuric acid are added if the after-treatment is carried out in a separate bath.

We mention in this place also those colours which are after-treated with copper sulphate, such as *Alizadine black* (Holliday), *Copper blue*, *Cyprus blue*, and *Cyprus green* (pp. 543 and 556), which, however, are not fast to milling, and serve chiefly for piece dyeing.

The after-chroming may be carried out in a separate bath, in which case some acid is added together with the chrome; but, generally, chroming in the dye-bath is preferred.

In the case of dyestuffs which are precipitated by calcium salts, it is well, before adding the dyestuff, to correct calcareous water by the addition of about 300 to 600 grms. (3 to 6 lbs.) ammonium oxalate per 1,000 litres (1,000 galls.) liquor.

Copper vessels should not be polished, the coating produced by the ordinary use of the vessel diminishing considerably the detrimental effect of the metal on the colours. In the case of dyestuffs very sensitive to its action, copper vessels are first prepared at 50° C. with  $\frac{1}{2}$  per cent. ammonium sulphocyanide (of the weight of the wool to be dyed), and after this liquor has been allowed to act for about twenty minutes, the dyestuff, sodium sulphate, and acid are added. A protective coating of sulphocyanide of copper seems to be produced by this treatment.

For subsequently shading the acid chrome colours after they have been fixed with chrome, the same colours may be used, especially in the case of loose wool, the dye-bath being slightly cooled off, and after addition of fresh dyestuff gradually brought to the boil, and boiled for twenty to thirty minutes. If only small quantities of colouring matters are subsequently added (not exceeding a quarter of the original quantity), a repeated chroming may be dispensed with.

A number of ordinary acid colours fast to milling, such as *Patent blue A*, *Brilliant milling green B*, *Sulphone cyanin*, *Fast acid violet*, *Formyl violet*, *Milling yellow*, *Sulphone yellow*, &c., may also be used for shading by adding them, along with the acid chrome colours, to the bath as well as after the dye has been chromed.

In the same way a great number of acid levelling dyestuffs may be employed, especially for subsequently shading the chromed colours on yarns and piece goods—*e.g.*, the various brands of *Patent blue*, *Cyanol*, *Cyanol fast green*, *Fast green*, *Alkali fast green*, *Naphthalene green*, *Acid violet*, *Azo-carmine*, *Rosinduline*, *Lanafuchsin*, *Azo-grenadin*, *Sorbin red*, *Tartrazin*, *Flavazin*, *Fast light yellow*, *Orange*, &c. The quantity to be used of such levelling colours should not be so large as to deteriorate the fastness of the dyed shade.

The dye-bath used for dyeing and subsequent chroming may be used for dyeing and chroming further lots. In order to exhaust the chrome remaining in the old liquor, it is well to boil the wool in the same for twenty to thirty minutes before adding fresh dyestuff.

A variation of the general method of dyeing acid chrome colours is that

with the use of the *Metachrome mordant* (Berlin),\* which mordant is a mixture of yellow chromate with ammonium sulphate. The bath is prepared with 3 per cent. or more *Metachrome mordant* and with the requisite quantity of dyestuff, and after entering the wool at a temperature not less than 60° C., the bath is brought to the boil, and heated until it is only slightly yellow, and then for one hour more; this prolonged boiling is necessary to develop and fix the colours well. In the hot dye-bath the ammonium salt is gradually decomposed, ammonia escaping, and sulphuric acid being liberated so as to act on the dyestuff and the neutral chromate (see the similar application of ammonium salts for fixing acid colours, p. 514). Yarns or piece goods are best boiled first with two-thirds of the required amount of *Metachrome mordant* for a half to three-quarters of an hour, and after neutralising the bath with ammonia, the rest of the mordant and the required colouring matters are added, and dyed as above. Soft water is to be preferred for this process; hard water should be boiled with the mordant for some minutes before adding the dyestuffs.

The method is employed for the various *Metachrome colours* (Berlin)—e.g., *Metachrome brown B paste*, *Metachrome bordeaux B and R paste*, *Metachrome yellow R paste*, *Metachrome yellow D, R D, 2 R D powder*, *Metachrome orange R double paste*, which may be shaded with *Cyprus green B* (p. 556), *Indocyanine B* (p. 552), and others. These dyestuffs yield colours of excellent fastness to light, milling, washing, acids, and alkalis, and are very valuable for the dyeing of loose wool, tops, yarns, and piece goods.

Another variation of a similar kind is the so called *chromate method* proposed by L. Cassella & Co. The bath is prepared with the necessary quantity of dyestuff and bichromate of potash or soda (about a half to two-thirds of the weight of dyestuff), and, in addition, 10 per cent. Glaubersalt for piece goods. The dyestuff and the bichromate are added separately to the dye-liquor. The material is entered at 70° to 80° C., and the bath brought to the boil within a quarter of an hour, and boiled for three-quarters of an hour. It is then exhausted by the addition of 2 to 3 per cent. acetic acid 30 per cent. (8° Tw.), and continued boiling for three-quarters to one and a quarter hours.

This method is employed for the various *Anthracene chromate colours* (Cassella)—e.g., *Anthracene chromate brown E B and S G*, *Anthracene chromate green B*, *Anthracene chromate blue X R*, *Anthracene chromate violet X B*, *Anthracene yellow C and B N*, &c., which may be shaded with *Diamine fast red F* (p. 391), *Wool red B* (p. 532), *Brilliant milling green B* (p. 555), *Alpha-naphthol blue*, and others. The colours are also very well adapted for dyeing loose wool, tops, yarns, and pieces, and possess excellent fastness to light, milling, washing, acids, and alkalis.

**Dyeing of Silk.**—Silk may be dyed like wool with the acid chrome colours. Since, however, the silk fibre is more sensitive to the action of chromic acid, such dyestuffs should be preferred as do not require heavy chroming to be developed and fixed, and which practically possess the same shade before and after chroming.

The dyeing is usually carried out with the addition of 2 to 5 per cent. acetic acid, beginning at 40° to 50°, raising to the boiling temperature, and exhausting the liquor with some sulphuric acid. For chroming, 1 to 2 per cent. bichromate, or 1 to 3 per cent. chromium fluoride, with the addition of 5 to 8 per cent. acetic acid are used; the silk is worked for a quarter of an hour in the boiling hot bath and then rinsed and brightened.

The acid chrome colours may be used in silk dyeing if colours fast to washing are required. They are, however, not very frequently employed in silk dyeing

\* English Patent 8874, 1900; *Journ. Soc. Dyers and Col.*, 1901, p. 67.

Numerous *acid chrome colours* yielding all kinds of shades are furnished by the various aniline colour works. They more or less resemble each other, being applied practically in the same way. Since the chemical constitution of most of these products has not yet been disclosed, we refrain from enumerating them, and shall only describe those the constitution of which we are in a position to communicate.

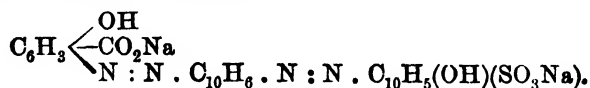
The principal method of dyeing has been indicated on p. 631. It may be noted that most of these dyestuffs can also be dyed very well on chromed wool, and the blue acid chrome colours especially are frequently employed in this way in order to produce brighter shades; frequently the colours dyed on chromed wool are gently after-chromed so as to improve the fastness to milling.

Name of Colours.	Makers.
Acid alizarin colours,	M. L. B.
Acid anthracene "	Bayer.
Acid chrome "	"
Alizarin azo "	Durand.
Anthra chrome "	Leonhardt.
Anthracene acid "	Cassella.
Anthracene chrome colours,	"
Anthracene chromate "	"
Anthracyl chrome "	Dahl.
Chrome fast "	Ch. Ind. Basle, Berlin.
Diamond "	Bayer.
Domingo alizarin "	Leonhardt.
Domingo chrome "	"
Erio chrome "	Geigy.
Meta chrome "	Berlin.
Omega chrome "	Sandoz.
Oxy chrome "	Oehler-Griesheim.
Palatine chrome "	B. A. S. F.
Salicine "	Kalle.

Attention may also be called to the *Chromotropes* discussed on p. 532, which may also be classed as "Acid chrome colours," and in addition various other "Acid colours" and Alizarin colours (see pp. 602, 605, 606, 611, *et seq.*).

The following dyestuffs, the constitution of which has been disclosed, may be briefly described.

#### DIAMOND BLACK F (Bayer).



For the production of Diamond black F aminosalicic acid is diazotised and combined with alpha-naphthylamine; the product is rediazotised and combined with alpha-naphtholsulphonic acid N W.

Brownish-black powder; aqueous solution, blue-violet; HCl, violet precipitate; NaOH, turns the solution blue; solution in H<sub>2</sub>SO<sub>4</sub>, green; on diluting, violet precipitate.

*Application.*—Diamond black chiefly serves for dyeing wool together with bichromate by the one-bath method. Dye with the addition of 4 to 5 per cent. acetic acid and 10 per cent. Glaubersalt, enter at 70°, heat to the boil, boil for three-quarters of an hour, and exhaust the bath with 2 to 2½ per cent. sulphuric acid within half an hour; add 1½ to 2 per cent. bichromate and work, boiling for thirty to forty minutes. The commercial product being disposed to frothing, it is well to boil it in the half-filled dye-vessel, together with the acetic acid, and then only to fill up with water.

The black produced in this way is very fast to light, milling, acids, and alkalies. White cotton is stained on milling; in order to produce colours which do not stain cotton, the chroming may be effected with a mixture of  $1\frac{1}{2}$  per cent. bichromate and 2 to 3 per cent. copper sulphate. When dyeing with acetic acid alone instead of using sulphuric acid a more bluish-black is obtained which, however, is not quite so fast to milling. Very good and fast blacks are also obtained by the use of formic acid, the dyeing being started with  $\frac{1}{2}$  per cent. formic acid 85 per cent. and  $3\frac{1}{2}$  per cent. being added for exhausting the dye.

The mordanting and dyeing, or two-bath method, yields blacks of a more violet caste, which are also less fast to milling than those obtained by the one-bath method.

Diamond black F is the chief brand represented by the above formula, and yields a jet-black by the one-bath method. The brands B B, G A, and N G produce more bluish shades of black, and N R a reddish shade of black of equally good fastness.

Silk may be dyed like wool, the quantity of bichromate being reduced to 1 per cent. in order to preserve the quality of the silk. The colour is very fast to light, washing, water, alkalies, acids, and stoving.

*Acid chrome blacks*, similar to or identical with this series of Diamond black, are:—

- DIAMOND BLACK (B.A.S.F., Berlin, Leonhardt, &c.).
- ANTHRACENE ACID BLACK (Cassella).
- BRILLIANT CHROME BLACK (Poirrier).
- ERA BLACK (Levinstein).
- ERIO CHROME BLACK A (Geigy).
- FAST CHROME BLACK (Chem. Ind. Basle, Holliday, &c.).
- SALICINE BLACK D (Kalle).

#### DIAMOND BLACK P V (Bayer).

o Aminophenol sulphonic acid—1 : 5 dioxynaphthalene.

Brown powder; aqueous solution, bluish-red; HCl, dark red precipitate; NaOH, no change; solution in  $H_2SO_4$ , blackish-green; on diluting, reddish precipitate.

*Application*.—This brand is valuable for dyeing wool fast to potting. Prepare the bath with  $2\frac{1}{2}$  per cent. acetic acid, dye, boiling fifteen to twenty minutes, add  $2\frac{1}{2}$  per cent. sulphuric acid, boil again for fifteen to twenty minutes and allow to feed for half an hour without steam, and add 2 to  $2\frac{3}{4}$  per cent. bichromate, boiling thirty to forty minutes. When dyeing in copper vessels it is well to add  $\frac{1}{4}$  grm. ammonium sulphocyanide per litre of liquor ( $\frac{1}{4}$  oz. per 100 galls.). Diamond black P V dyes a jet-black, equalling the "F" brand (p. 634) in fastness, while, in addition, it is fast to potting, and does not stain white cotton on milling.

DIAMOND BLACK P V B and P 2 B (Bayer) are similar to the "P V" brand and dye more bluish shades of the same fastness.

#### ANTHRACENE CHROME BLACK 5 B and F (Cassella).

These are azo-compounds of diazotised (2 : 3) aminonaphthol sulphonic acid.

Brown powder; aqueous solution, dark violet; HCl, readily soluble red-violet precipitate; NaOH, readily soluble precipitate, forming a blue-violet solution; solution in  $H_2SO_4$ , blackish-blue (F) or red-violet (5 B); on diluting red-violet solution and precipitate.

*Application*.—Anthracene chrome black is dyed on wool only and is always chromed after dyeing. Calcareous water should be corrected with

ammonium oxalate when using the "F" brand. Dye with the addition of 5 per cent. acetic acid, boiling a half to three-quarters of an hour, add  $1\frac{1}{2}$  to  $2\frac{1}{2}$  per cent. sulphuric acid in two portions, boil until the bath is nearly decolourised, and finally chrome with  $1\frac{1}{2}$  to  $2\frac{1}{2}$  per cent. bichromate, boiling gently. When chroming in a separate bath add 2 per cent. hydrochloric acid to dissolve a deposit of calcium oxalate. The black is developed by the chroming, the direct colour being dull violet. If too much sulphuric acid is used the black will lose its fine bloom. Anthracene chrome black 5 B may also be dyed with formic acid (p. 635). Anthracene chrome black F dyes a very fine jet-black without a reddish cast, similar to logwood black and not changing its tone in artificial light. The "5 B" brand dyes a more greenish-black, which is also very fine, especially in deep shades. Both brands are very fast to light, milling, alkalis, and acids; they resist acid cross dyeing, and on milling they do not stain white cotton. Anthracene chrome black F is fairly fast to potting, but the "5 B" brand is perfectly fast in this respect.

ANTHRACENE CHROME BLACK F E resembles the "F" brand and yields deeper shades of black.

ANTHRACENE CHROME BLACK P EXTRA, PPN EXTRA, and other "P" brands behave like Anthracene chrome black 5 B, especially in fastness to potting.

*Acid chrome blacks* of very good fastness to *potting* are also:—

CORVAN BLACK B, B G, T (B.A.S.F.).

CHROMATE BLACK P F, P B, P 4 B, P T (Berlin).

ERIO CHROME BLACK P (Geigy).

PALATINE CHROME BLACK F (B.A.S.F.). ACID ALIZARIN BLACK S E (M.L.B.).

oo Diaminophenyl sulphonic acid  $\left\{ \begin{array}{l} \text{beta-naphthol} \\ \text{beta-naphthol.} \end{array} \right.$

Brown-black, sparingly soluble powder or paste; aqueous solution, dark blue; HCl, red precipitate; NaOH, greenish-blue precipitate; solution in  $H_2SO_4$ , violet; on diluting, red precipitate.

*Application*.—This dyestuff is also principally used for dyeing wool by the after-chroming method, but can be dyed fairly well on chromed wool by the two-bath method. The dyestuff should be mixed well with cold condensed water and added through a fine sieve to the dye-bath. Calcareous water should be corrected by the addition of ammonium oxalate (p. 632). Dye with the addition of 10 per cent. Glaubersalt, add 4 to 8 per cent. acetic acid, heat to the boil and boil for half an hour, add after half an hour 2 to 4 per cent. acetic acid or 1 to 2 per cent. sulphuric acid, boil half an hour longer, and chrome, boiling half an hour with  $1\frac{1}{2}$  per cent. bichromate. Palatine chrome black F, or Acid alizarin black S E, dyes a bloomy black of excellent fastness to light and very good fastness to milling, alkalis, acids, and stoving.

PALATINE CHROME BLACK S (B.A.S.F.). ACID ALIZARIN BLACK S N (M.L.B.).

These dyestuffs closely resemble the preceding two brands. They are distinguished by better solubility, and may be dyed with sulphuric acid instead of acetic acid.

In addition to the preceding, a great number of brands of very similar properties, such as *Palatine chrome black FN, FT, L, LN*, Acid alizarin black S E T, S N T, &c., are found in commerce.

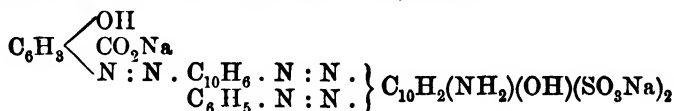
Acid chrome blacks, more or less resembling the preceding brands in general tinctorial properties and fastness, are furnished to the trade by most aniline colour works.

**DIAMOND GREEN** (Bayer).

This dyestuff is produced like Diamond black F, 1 : 8 dioxynaphthalene (4) sulphonic acid being used as component in place of alpha-naphthol sulphonic acid N W.

Reddish glittering powder; aqueous solution, blue; HCl, violet precipitate; NaOH, red-violet solution; solution in  $H_2SO_4$ , dark green; on diluting, blue precipitate.

*Application and Properties.*—Same as Diamond black F (p. 634). Diamond green dyes in combination with chromium mordants dark green (Russian green) of excellent fastness to light, milling, alkalies, and acids, and serves principally for shading purposes.

**CHROME PATENT GREEN A and N** (Kalle).

Chrome patent green is produced by combining diazo-salicylic acid with alpha-naphthylamine or alpha-naphthylamine sulphonic acid Cl, diazotising the product and combining the same, and also diazo-benzene with 1 : 8 aminonaphthol (4 : 6) disulphonic acid K.

Violet-brown powder; aqueous solution, red-brown; HCl, blue-black soluble precipitate; NaOH, blue solution; solution in  $H_2SO_4$ , black-green; on diluting, greenish-blue solution and black precipitate.

*Application.*—Chrome patent green is dyed on wool with the addition of 4 per cent. acetic acid, exhausting the bath with 1 per cent. sulphuric acid, and chroming with  $1\frac{1}{2}$  per cent. bichromate. It dyes a fairly bright, dark bluish-green of very good fastness to light, milling, alkalies, and acids.

**CHROMOGENE I** (M.L.B.).

Chromogene I is the colourless sodium salt of (1 : 8) dioxynaphthalene (3 : 6) disulphonic acid, the so-called chromotrop acid which, by oxidation with bichromate, is converted into an exceedingly fast brown colour.

White powder; aqueous solution, pale brown; HCl or NaOH, no change; solution in  $H_2SO_4$ , colourless; on diluting, no change.

*Application.*—Chromogene I serves for dyeing wool brown. Dyed direct it does not colour the wool, nor can it be used for dyeing mordanted wool, since it requires severe prolonged chroming with bichromate and sulphuric acid. Dye boiling one hour with the addition of 4 per cent. sulphuric acid and 10 per cent. Glaubersalt, add 3 per cent. bichromate and 1 per cent. sulphuric acid, boiling again not less than one to one and a-half hours to develop the colour completely and evenly. A yellowish, not very full, brown is obtained, which is of excellent fastness to light, milling, alkalies, and acids, and which is well adapted for light and medium *mode* shades.

**SULPHAMINE BROWN** (Dahl). **NAPHTHINE BROWN** (Poirrier).

Sulphamine brown A or Naphthine brown  $\alpha$  is produced by the action of diazotised alpha-naphthylamine upon the sodium bisulphite compound of nitroso beta-naphthol and Sulphamine brown B or Naphthine brown  $\beta$  by using beta-naphthylamine in place of the alpha-compound.

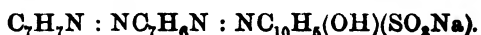
*Sulphamine Brown A.*—Red-brown powder; aqueous solution, red-brown; HCl, brown precipitate; NaOH, brown precipitate; solution in  $H_2SO_4$ , black green; on diluting, brown precipitate.

*Sulphamine Brown B.*—Solution in  $H_2SO_4$ , violet; otherwise the reactions are similar to those of the "A" brand, but more yellowish.

*Application.*—Sulphamine brown or Naphthine brown is not an acid chrome dyestuff in the exact meaning of the term, but it may be described

here, since it can be after-treated with bichromate. Sulphamine brown A dyes on wool, with the addition of 5 to 10 per cent. sodium bisulphate, a fine reddish-brown, and the "B" brand a yellow-brown of fairly good fastness to light and milling, and good fastness to alkalis and acids; by treatment with  $2\frac{1}{2}$  to 5 per cent. copper sulphate, these are converted into very deep bluish-browns of slightly greater fastness to light and milling. The after-treatment may also be carried out with a mixture of 2 to 3 per cent. bichromate, and  $2\frac{1}{2}$  to 5 per cent. copper sulphate. Sulphamine brown may also be dyed with the addition of acetic acid on chromed wool, and after-treated with copper sulphate. Silk is dyed in boiled-off liquor acidulated with sulphuric acid, and after-treated with copper sulphate. A deep brown very fast to water is thus obtained on silk.

CLOTH-RED G (Oehler). CLOTH-RED G EXTRA (Bayer). CLOTH-RED G A (Berlin).



Cloth-red G is an acid azo-dyestuff produced by the action of diazotised aminoazotoluene on beta-naphthol sulphonic acid S.

Red-brown powder, which dissolves sparingly in water with a brown-red colour; HCl, brown-red precipitate; NaOH, yellowish-brown precipitate which dissolves in pure water; solution in  $H_2SO_4$ , blue; on diluting, brown-red precipitate. The lakes, which the salts of the alkaline earth form with Cloth-red, are soluble in water containing 1 per cent. of tannic acid, which explains why the addition of sumach is advantageous when dyeing with hard water.

*Application.*—Cloth-red is used in wool-dyeing and is fixed with the aid of chromium mordants, either alone or associated with tannin. It can also be dyed by the methods used for the acid colours, and thus yields a bluish-red shade. It is an excellent substitute for the red woods, as it combines well with the natural dyestuffs—*e.g.*, logwood or fustic—and can be saddened with copper and iron salts, giving rise to a variety of shades. The credit of having introduced this dyestuff as a fast mordant colour is due to F. V. Kallab.

For the production of very fast colours the process of separate mordanting and dyeing is most satisfactory: Boil the wool for  $1\frac{1}{2}$  to two hours with 3 per cent. of potassium bichromate and 3 per cent. of sulphuric acid or—for mixed shades in conjunction with wood colours—boil with 3 per cent. of bichromate,  $1\frac{1}{2}$  per cent. of copper sulphate, and  $1\frac{1}{2}$  to 3 per cent. of sulphuric acid. A smaller quantity of sulphuric acid produces shades which are not quite fast to milling. Deep shades require a greater quantity of mordant to resist milling perfectly.

After mordanting, the goods should be well rinsed in water.

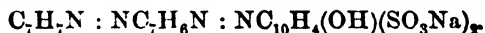
For dyeing, no calcareous water should be used or some tannic acid or sumach should be added (see above). The dyestuff is dissolved in hot water and passed through a fine hair sieve into the dye-bath; for mixed shades the decoction of sumach, fustic, and logwood is boiled first and then the Cloth-red is added. Light shades require the addition of a little ammonia or (for dyeing in copper vessels) of sodium acetate to the dye-bath to dye evenly and well through. For dark red shades the addition of 1 part of acetic acid to 1000 parts of water is of advantage, since it prevents too rapid dyeing. If a great quantity of dyestuff is required, only one-half is added at first and the rest after some time. The goods are introduced at  $40^\circ$ , the bath is gradually heated to the boiling point, and this temperature is maintained for about one hour; towards the end of the dyeing some acetic acid may be added to deepen the shade. The colour can be made faster to milling by adding 3 per cent. of stannic chloride to the exhausted dye-bath and boiling up. Wood colours which have been dyed in one bath with Cloth-red can be saddened with iron

or copper salts as usual. Alum must not be added to the bath, until the Cloth-red is all taken up by the fibre, since this dyestuff is precipitated thereby. Fresh colour can be added even after the saddening and dyes evenly; but the dye-liquor should first be cooled down a little. Cloth-red G dyes on chrome-mordanted wool a full bluish-red shade, which is very fast to light and to milling.

Cloth-red can also be fixed in a single bath with chromium fluoride or with bichromate; for 1 part of colour 1 to  $1\frac{1}{2}$  parts of chromium fluoride or bichromate are used. The method is useful for goods which do not require strong milling, but the colours of which require to be fast in wearing. In this way Cloth-red combines well with the acid chrome colours.

Cloth-red dyes in one bath with the addition of some tannin—*e.g.*, 5 per cent. of the weight of the wool of sumach extract (56° Tw.). The shades thus obtained are fast to light, but become bluer on milling; they can however, be saddened with sulphate of copper or iron, and the effect of milling can thus be somewhat counteracted. Very dark claret-red shades are produced by the addition of logwood, and, if fustic is also added, a very fast brown will be obtained. Brown in one bath is produced by dyeing at the boil with sumach, fustic, and Cloth-red for one and a-half hours, cooling a little, adding sulphate of copper, and boiling three-quarters of an hour, cooling again, saddening with sulphate of iron, boiling three-quarters of an hour, and finally washing.

**CLOTH-RED B** (Oehler). **CLOTH-RED O** or **FAST BORDEAUX O** (M.L.B.). **CLOTH-RED B A** (Berlin). **FAST MILLING RED B** (Levinstein).



Cloth-red B is analogous to Cloth-red G in constitution, and is produced by the action of diazotised aminoazotoluene on beta-naphthol disulphonic acid (R salt)

Brown-red powder, sparingly soluble in water with a crimson colour; HCl, brown precipitate; NaOH, claret-red precipitate soluble in pure water; solution in  $H_2SO_4$ , blue; on diluting, brown-red precipitate. In its general character, Cloth-red B strongly resembles Cloth-red G.

*Application and Properties.*—Same as Cloth-red G. Cloth-red B produces a bluer and purer claret-red on wool.

**CLOTH-RED B** (Bayer, Dahl).

Azo-dyestuff produced from aminoazotoluene and alpha-naphthol monosulphonic acid NW, isomeric with Cloth-red G (Oehler).

Brown powder, sparingly soluble in water; the aqueous solution is crimson red; HCl, red precipitate; NaOH, soluble bluish-red precipitate; solution in  $H_2SO_4$ , blue; on diluting, crimson precipitate.

*Application and Properties.*—Same as Cloth-red G.

**CLOTH-RED 3 G** (Bayer.) **CLOTH-RED 3 G A** (Berlin).

Azo-compound produced from aminoazotoluene and beta-naphthylamine sulphonic acid Br, isomeric with Cloth-red G (Oehler).

Brown-red powder, dissolving in water with a red colour; HCl, dark red-brown precipitate; NaOH, does not readily precipitate the colour; solution in  $H_2SO_4$ , greenish-blue; on diluting, dark red-brown precipitate.

*Application and Properties.*—Same as Cloth-red G (Oehler). The shade is a more yellowish-claret.

**CLOTH-RED G** (Bayer). **AZO-COCCIN 7 B** (Berlin). **CLOTH-RED R** (Dahl). **FAST RED 7 B** (Chemikalien Werk, Griesheim).



This Cloth-red G is different from the original Cloth-red G introduced



by K. Oehler. It is the azo-compound obtained from aminoazobenzene and alpha-naphthol sulphonic acid N W.

Brown powder, which is not readily soluble in water; aqueous solution, dark crimson; HCl, brown-red precipitate; NaOH, soluble red-violet precipitate; solution in  $H_2SO_4$ , blue; on diluting, brown-red precipitate.

*Application and Properties.*—Same as Cloth-red G (Oehler)

**CLOTH SCARLET G** (Kalle).

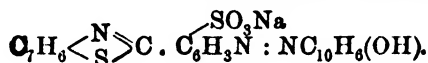
Aminoazobenzene sulphonic acid—beta-naphthol.

Brown-red powder; aqueous solution, orange-red; HCl, dark precipitate, soluble with a red colour; NaOH, soluble brown precipitate; solution in  $H_2SO_4$ , green; on diluting, yellowish-red solution and precipitate.

*Application.*—Same as Cloth-red. Cloth scarlet G dyes on wool in an acid bath a fairly bright scarlet, fairly fast to light and milling, and fast to alkalis and acids, which by subsequent chroming or by dyeing on chromed wool becomes still faster to milling.

**CLOTH SCARLET R** (Kalle) is the corresponding aminoazotoluene compound which possesses similar reactions and properties and dyes a bluish-red of equal fastness to that of Cloth-scarlet G.

**CLAYTON CLOTH-RED** or **STANLEY RED** (Clayton).



Clayton cloth-red is the product of the reaction of diazotised dehydrothio-*paratoluidine* sulphonic acid with beta-naphthol.

Dark red granular powder which dissolves in hot water with a clear scarlet colour; HCl, orange precipitate; NaOH, precipitates the dyestuff completely; solution in  $H_2SO_4$ , violet; on diluting, red precipitate.

*Application.*—Clayton cloth-red can be dyed on wool as a direct acid colour, or on a chromium mordant in the same way as the preceding Cloth-reds. When dyed without mordants it produces a full blue shade of scarlet, which is fairly fast to light and milling. Dyed on chromed wool it possesses good fastness to milling, the shade does not differ much in appearance from the colour dyed without mordant.

**EMIN RED** (Berlin).

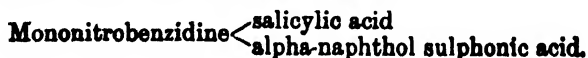
Isodehydrothiometylidine—beta-naphthol sulphonic acid S.

Red powder; aqueous solution, yellowish-red; HCl, red precipitate; NaOH makes the solution more yellowish; solution in  $H_2SO_4$ , crimson; on diluting, red precipitate.

*Application.*—Emin red dyes on wool in a bath acidulated with acetic acid, a bright yellowish-red fairly fast to light and milling and good to acids and alkalis. By subsequent fixing with 1 to 3 per cent. chromium fluoride in a boiling bath, the colour becomes faster to milling, but a little duller. Emin red may also be dyed very well by the two-bath method on chromed wool. Emin red is closely related to Erika (p. 395), a direct cotton colour, and like this it dyes cotton fairly well; when dyed on wool it, therefore, bleeds on milling into white cotton, although it does not affect white wool.

Silk is dyed with Emin red in an acid bath; the colour possesses good fastness to water and washing.

**ANTHRACENE RED** (Ch. Ind. Basle, Bayer).



Brown-red powder; aqueous solution, red; HCl, red precipitate; NaOH, no change; solution in  $H_2SO_4$ , crimson; on diluting, brown-red precipitate.

*Application.*—Anthracene red dyes on wool in an acid bath, a bluish-scarlet of fairly good fastness to light, acids, and alkalis, which by subsequent chroming with bichromate becomes very fast to milling. It may also be dyed on chromed wool. Anthracene red dyes silk in an acid bath, a scarlet very fast to light and washing.

**SALICINE RED B, G, G G** (Kalle) is similar to the preceding Anthracene red in chemical constitution and properties. Salicine red B dyes a bluish-scarlet, G a yellowish one, and G G a still more yellowish-scarlet.

**DIAMINE FAST RED F** (Cassella).

This dyestuff, which belongs to the direct cotton colours (see p. 391), is also extensively used in wool dyeing, both by the after-chroming method or by the two-bath method and recently also by the chromate method (p. 633). It dyes madder-red shades of very good fastness to light, milling, alkalis, acids, stoving, and rubbing.

**MILLING ORANGE** (Dahl).

Aminoazobenzene sulphonic acid—salicylic acid.

Brownish-yellow powder; aqueous solution, brown; HCl, sparingly soluble, gelatinous, brownish-yellow precipitate; NaOH, deep red solution; solution in  $H_2SO_4$ , red-violet; on diluting, brown precipitate.

*Application.*—Milling orange dyed on wool in an acid bath and chromed with bichromate dyes a reddish-orange of very good fastness to light, milling, acids, and alkalis. It may also be dyed on chromed wool; the colour, however, is then not quite fast to milling, unless slightly after-chromed. The shade of the direct colour is more yellowish than in combination with chromium mordants. On chromed silk an orange fast to soap and water is obtained.

**ALIZARIN YELLOW G G or G G W** (M.L.B.).



Alizarin yellow G G is produced by the action of diazotised metanitriline on salicylic acid. Light yellow powder (G G W), or yellow paste containing 20 per cent. of dry colouring matter (G G); the former is readily soluble in water with a yellow colour, the latter is only slightly soluble. Both dissolve in caustic soda with an orange-red colour, but are precipitated by an excess in the form of a soluble yellow precipitate; hydrochloric acid produces in the solutions yellow precipitates. The solution in sulphuric acid is yellow, and yields on diluting with water a yellow precipitate.

*Application.\**—Alizarin yellow G G serves as a substitute for Persian berries in calico-printing, and as a substitute for fustic in wool dyeing. It produces a greenish-yellow shade on chromium mordants, and a beautiful golden yellow on alumina; but the former only is fast enough to soap to be employed.

**Cotton.**—Alizarin yellow G G is dyed on cotton which has been mordanted with chromium by any of the usual methods (p. 566). Chromium mordant G A I, diluted with three to four times its weight of water, is recommended by the makers; the goods are padded in this solution, dried, and passed at 60° through a solution of soda ash (6 parts in 1,000 of water); after washing, the goods are dyed in a bath containing acetic acid, starting cold, and raising to 90°; it is advantageous to steam them for an hour after dyeing. For dyeing on an aluminium mordant calcareous water is required.

\* R. Nietzki, *Journ. Soc. Dyers and Col.*, 1889, p. 175.

Wool may be dyed by the single-bath, by the after-chroming, or by the chromate method (p. 568), or after previous chroming with bichromate, with Alizarin yellow G G. An olive-yellow shade, similar to that of old fustic, is obtained which is very fast to light and milling.

Alizarin yellow G G can also be dyed on wool in an acid bath in the same way as the acid colours; but when thus applied, has considerably less colouring power than on metallic mordants; the yellow shade is very fast to light.

**ALIZARIN YELLOW R** (M.L.B., Bayer). **TERRA-COTTA R** (Geigy)

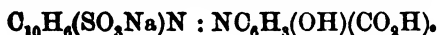
Alizarin yellow R is isomeric with the preceding compound, being produced from para-nitraniline and salicylic acid.

Light brown paste containing 20 per cent. of dry colouring matter, which is sparingly soluble in water; it dissolves with a deep red colouration in caustic soda solution, but is precipitated by an excess in the form of a soluble reddish-yellow precipitate; hydrochloric acid produces in the solution a brownish-yellow precipitate. The solution in sulphuric acid is red, and yields a brownish-yellow precipitate on diluting with water.

*Application and Properties.*—Same as Alizarin yellow G G.

Alizarin yellow R produces a full brown-orange shade on chromium mordants.

**MILLING YELLOW** (Dahl). **ANTHRACENE YELLOW B N** (Cassella).  
**CHROME YELLOW D** (Bayer). **CHROME FAST YELLOW** (Berlin). **MORDANT YELLOW G** (B.A.S.F.). **MORDANT YELLOW O** (M.L.B.).

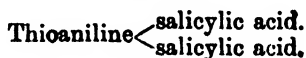


Milling yellow (Dahl) is an azo-compound produced by the reaction of diazotised betanaphthylamine-alphasulphonic acid with salicylic acid. The other products are identical or prepared with isomeric sulphonic acids.

Yellow or brown-yellow powder; aqueous solution, yellow; HCl, redder solution and soluble reddish precipitate; NaOH, yellowish-brown or brownish-red; solution in  $\text{H}_2\text{SO}_4$ , yellowish-brown or brownish-red; on diluting, a soluble yellow or reddish precipitate forms gradually.

*Application.*—Milling yellow is one of the most generally employed mordant yellows for wool. It is dyed like Alizarin yellow and especially so by the after-chroming method, and it is highly valued for its solubility and good levelling power. Dyed direct it dyes reddish-yellow shades very fast to light and fairly fast to milling. In combination with chromium mordants it produces olive-yellow shades, which are similar to those of old fustic and possess very good fastness to light, milling, acids, and alkalis. Dyed on silk and subsequently chromed, it yields olive-yellows very fast to light and washing.

**ANTHRACENE YELLOW C** (Cassella).



Brown-yellow powder or paste, not very freely soluble; aqueous solution, pale yellow-brown; HCl, yellowish-grey precipitate; NaOH, sparingly soluble yellowish-red precipitate; solution in  $\text{H}_2\text{SO}_4$ , dark red-violet; on diluting, yellowish-grey precipitate.

*Application.*—Anthracene yellow C is best dyed on wool with acetic acid and subsequently chromed with bichromate or dyed by the chromate method, and produces an olive-yellow fuller than the preceding Anthracene yellow B N and of excellent fastness to light, milling, alkalis, and acids. The colour on chromed wool is of nearly the same fastness to milling. Dyed direct a reddish-yellow of excellent fastness to light and very good fastness to washing is obtained. Silk is dyed with the addition of acetic acid and fixed with

chromium fluoride or bichromate; an olive-yellow very fast to light and washing is obtained in this way.

**FAST MORDANT YELLOW C** (B.A.S.F.) is similar to or identical with the preceding dyestuff.

**DIAMOND YELLOW G** (Bayer).



Diamond yellow G is produced by combining diazotised meta-aminobenzoic acid with salicylic acid. It is sold as a greyish-yellow paste, which dissolves sparingly with a yellow colour in water, but is readily soluble in a solution of soda or of sodium acetate; hydrochloric acid produces a yellow precipitate in the alkaline solutions. The solution in sulphuric acid is reddish-yellow, and gives, on diluting with water, a yellow gelatinous precipitate.

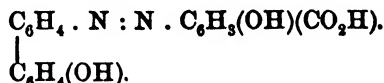
*Application.*—Diamond yellow G is used in the same way as the preceding yellow colouring matters as a fustic substitute for the dyeing of wool mordanted with chromium mordants, and especially as a substitute for Persian berries in calico printing. It combines well with other mordant colours and yields very fast shades resembling those obtained with old fustic.

**DIAMOND YELLOW R** (Bayer).

Diamond yellow R is isomeric with Diamond yellow G and is produced from orthoaminobenzoic acid and salicylic acid. It forms a brown paste, little soluble in water with a yellow colour, readily soluble in a solution of sodium acetate or soda. The solution in sulphuric acid is reddish-yellow; on diluting, a brownish-yellow precipitate is obtained.

*Application and Properties.*—Same as Diamond yellow G. It dyes a redder shade which is neither bright nor very full.

**DIAMOND FLAVIN G** (Bayer).



Diamond flavin G is produced by the action of 1 mol. tetrazotised benzidine on 1 mol. salicylic acid and boiling the intermediate compound.

Yellowish-green paste, sparingly soluble in pure water, dissolving on addition of sodium acetate; NaOH, dissolves with an orange or red-brown colour; HCl, dark yellow precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, claret; on diluting, dark yellow precipitate.

*Application.*—Same as Milling yellow. Diamond flavin G is chiefly dyed on wool by the after-chroming method and on chromed wool (by the two bath method), and yields olive-yellow shades similar in shade and fastness to Milling yellow or Chrome yellow D.

**CHROME FAST YELLOW G G** (Berlin).

*o* Anisidin—salicylic acid.

Greyish-yellow powder; aqueous solution, pale yellowish-brown; HCl, yellow precipitate; NaOH, redder solution and soluble precipitate; solution in H<sub>2</sub>SO<sub>4</sub>, yellowish-brown; on diluting, at first yellowish-red, then yellow solution and yellow precipitate.

*Application.*—Chrome fast yellow is used on wool in combination with chrome, either by dyeing in an acid bath and chroming with bichromate or by the two-bath method on chromed wool. It dyes a greenish-yellow of very good fastness to light, milling, acids, and alkalis.

**CHROME FAST YELLOW R** (Berlin).

Dyes a redder yellow of similar properties.

**CRUMPSALL YELLOW (Levinstein).**

$\beta$ -Naphthylamine  $\gamma$ -disulphonic acid—salicylic acid.

Yellow powder; aqueous solution, yellow; HCl, orange-red solution; NaOH, greenish-yellow solution; solution in H<sub>2</sub>SO<sub>4</sub>, orange-red; on diluting, little change.

*Application.*—Crumpsall yellow is dyed on wool by the after-chroming or by the two-bath method, and yields olive-yellow shades of good fastness to light, milling, acids, and alkalies.

**ALIZARIN YELLOW F S (Durand).**

This is diphenyl-tolyl-carbinol trisazo-tri-salicylic acid produced by the action of diazotised Magenta on salicylic acid.

Yellowish-brown, sparingly soluble paste; aqueous solution, yellow; HCl, brown precipitate; NaOH, redder solution, solution in H<sub>2</sub>SO<sub>4</sub>, dark bluish-green; on diluting, brown precipitate. Alizarin yellow F S by reduction is split up into Magenta and salicylic acid, the solution thereby being coloured pink or red.

*Application.*—Alizarin yellow F S yields when dyed with chromium mordants on wool or cotton olive-yellow shades of fairly good fastness. It is of special interest for the discharge style, because by reducing discharges it is discharged pink, Magenta being formed.\*

Erio chrome colours not detailed.

**MISCELLANEOUS COLOURS.**

The colours described under this heading have little similarity, chemically or tinctorially, either amongst themselves or with the preceding dyestuffs. They are not soluble in the ordinary solvents, and are produced in the fibre by various processes.

**ANILINE BLACK.**

Aniline black is the name given to an insoluble black dyestuff which is produced by the oxidation of aniline (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>) in an acid medium. If the oxidation is effected on the fibre, the colour, for reasons which are not known, becomes fixed, and the fibre is dyed a fast black. Although it is easy to produce Aniline black in the solid condition, the product is of no practical value as a dyestuff, there being no adequate means of applying it in dyeing in consequence of its insolubility in all solvents. In practice the colour is, therefore, invariably produced on the fibre.

It is not within the scope of this work to give a historical account of all the observations which have been made, and the researches which have been carried out, in connection with this most important colour, for details of which the reader is referred to other published accounts.† The first who appears to have noticed the formation of a colour approaching a black in shade from aniline was Runge,‡ who obtained a dark green colour on heating the nitrate in presence of copper chloride on a porcelain plate. Fritsche§ noticed that chromic acid added to solutions of aniline salt produced a dark green, and sometimes a blue-black precipitate. Three years later the same chemist produced a deep blue by the action of chlorate of potash and hydrochloric acid on aniline salt, and made an attempt to determine its composition.

\* J. Brandt, *Bull de Mulhouse*, 1898, p. 115.

† J. Lightfoot, *The Chemical History and Progress of Aniline Black*, 1871; F. Craze Calvert, *Dyeing and Calico Printing*, 1876; E. Noelting, *Histoire scientifique et industrielle du noir d'aniline*, and current literature.

‡ *Mon. Scient.*, 1863, p. 533.

§ *Journ. pr. Chem.*, 1840, p. 454.

Although Runge had the idea of producing colours on the fibre by the oxidation of aniline, it was not until 1860 that anything of a practical nature was suggested, when Calvert, Clift, and Lowe,\* by impregnating calico with chlorate of potash, and printing on an acid hydrochloride of aniline, obtained, on allowing the fabric to age, a green to which they gave the name "Emeraldine." By a subsequent treatment with bichromate of potash, the green changed to a deep Indigo blue, which was named by them Azurine. The process was, however, not of a sufficiently practical character to render its adoption on a large scale a success. At about the same time John Lightfoot, of Accrington, was engaged on the same subject. In his *Chemical History and Progress of Aniline Black*, he says (p. 1):—

"In the year 1859 I was working out some experiments upon aniline for Mr. Richard Dugdale Kay, of Accrington, which he had sent me as oil of naphtha; the market price of it was then from 15s. to 20s. per lb.

"In November of the same year I found that by mixing an acid chloride of aniline (equal parts of pure hydrochloric acid and aniline) with starch paste, holding 4 ozs. of chlorate of potash per gallon, and printing this mixture with a wood block, little or no colour was produced after twenty-four hours' ageing; but that when the same colour was printed in the machine with a copper roller, a green colour was produced in twelve hours.

"My notice of this strange fact was the cause that led me to the discovery of Aniline black. I at once repeated this mixture, and added to it various proportions of nitromuriate of copper, 88° Tw., and I then found that the intensity of the black was dependent upon the proportions of copper and aniline salt employed, as well as the duration of the ageing.

"The colour, when first printed, was a pale olive, which gradually developed into the fibre to an intense myrtle-green in about twenty-four hours. When washed in water *only*, without alkali or soap, it became an intense black."

Further on he states:—"The high price of aniline at this time prevented me thinking much of the black except as a chemical curiosity, but I had sufficiently developed the colour to print a few pieces of calico in July, 1860, at the Broad Oak Print Works, Accrington.

"Except a few pieces of single blacks, nothing more was done until the end of the year 1862, when an offer was made for the process by Messrs. J. J. Müller & Co., of Basle, Switzerland, which resulted in it being patented in January, 1863, and sold to them."

This, then, was the first technical Aniline black, and the credit of having rendered its application a practical success is undoubtedly due to Lightfoot.

The composition of Aniline black has been the subject of numerous investigations. Fritsche † attributed to the indigo-blue precipitate which he obtained by treating aniline salt with chlorate of potash in presence of free hydrochloric acid, the formula  $C_{24}H_{20}N_4Cl_2O$ . Armand Müller ‡ ascribed to the black obtained from aniline salt, copper sulphate, potassium chlorate, and ammonium chloride the formula  $C_{12}H_{14}N_2O_4$ . Goppelsroeder, § Kayser, || and Nietzki, ¶ all working independently of each other, concluded, however, that Aniline black was a compound free from oxygen, and that the composition of the base is represented by some multiple of  $C_6H_5N$ . By determining the amount of

\* English Patent No. 1426, 1860.

† *Journ. pr. Chem.*, 1843, p. 202.

‡ *Chem. Centralblatt*, 1871, p. 268.

§ *Jahresberichte*, 1876, p. 702.

|| *Verhandlungen d. Kgl. Gewerbevereins in Nürnberg*, 1877.

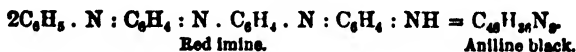
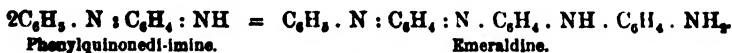
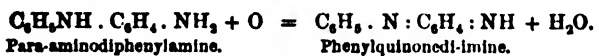
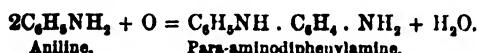
¶ *Berl. Ber.*, xi. (1878), p. 1094.

hydrogen necessary to reduce Aniline black to its leuco-compound, Nietzki\* found that 2 hydrogen atoms were added by  $C_{18}H_{15}N_3$ , and he concludes that this formula probably represents the composition of Aniline black. At the same time he admits † that it possibly contains less hydrogen, and might be represented as  $C_{18}H_{13}N_3$ .

Willstätter and Moore ‡ are also of opinion that the hydrogen given by previous investigators is too high, and regard Aniline black base as being represented by some multiple of  $C_6H_4N$ . By oxidising para-aminodiphenylamine,  $C_6H_5NH \cdot C_6H_4 \cdot NH_2$ , by means of dry silver oxide in ethereal solution, they succeeded in obtaining phenylquinoned-imine, §  $C_{12}H_{10}N_2$ , or  $C_6H_5 \cdot N : C_6H_4 : NH$ , in the form of light yellow crystals, melting point  $79^\circ$ , which are readily soluble in alcohol, ether, and benzene. In presence of aqueous hydrochloric acid this body at once passes into the hydrochloride of emeraldine. The base of emeraldine was found by analysis to correspond to some multiple of  $C_6H_5N$ , and a molecular weight determination showed this multiple to be 4, so that emeraldine has the composition  $C_{24}H_{20}N_4$ . On reduction, emeraldine gives a well-defined, colourless leuco-compound,  $C_{24}H_{22}N_4$ , which is readily oxidised by the air in presence of a trace of caustic soda back to emeraldine.

If a benzene solution of emeraldine is shaken with lead peroxide in presence of anhydrous sodium sulphate (as dehydrating agent), the solution becomes blood-red, and on concentrating yields small red crystals, melting point  $195^\circ$  to  $196^\circ$ , which possess the composition  $C_{24}H_{18}N_4$ , and thus represent an oxidation product of emeraldine formed by abstracting two atoms of hydrogen. By reducing agents this *red imine* is converted successively into emeraldine and the leuco-compound of emeraldine. By the action of dilute acids, or even by heating with water alone to  $150^\circ$ , this red imine is converted by polymerisation into Aniline black. Assuming that in this polymerisation two molecules of the red imine come together to form Aniline black, it is clear that the lowest molecular weight that can be ascribed to Aniline black would correspond to the formula  $C_{48}H_{31}N_8$ .

Thus, the successive stages by which aniline is converted into Aniline black might be represented by the following equations:—



\* *Chemie d. organ. Farbstoffe.*, 5th ed., p. 267.

† *L.c.*

‡ *Journ. Soc. Dyers and Col.*, 1906, p. 4.

§ This body had been previously obtained, though in an impure state, by H. Caro in 1896 (*Naturforscherversammlung, Frankfurt*) by the oxidation of an aqueous solution of aniline with permanganate of potash. Caro pointed out that it is reduced by stannous chloride to para-aminodiphenylamine, and that it yields emeraldine by mere contact with acids.

Having regard to the conditions of its formation, Willstätter and Moore state that technical Aniline black must in all cases contain a little chlorine and oxygen. Marsden\* gives the results of a series of experiments in which a known weight of pure aniline salt was treated with known amounts of chromic acid until the smell of aniline was displaced by that of quinone. The remaining aniline was estimated, as also the quantities of chromium oxide and chromic acid remaining in the precipitate. From the results thus obtained, which were confirmed by an ultimate analysis of the purified Aniline black, Marsden came to the conclusion that his black contained oxygen and that its composition was represented by a formula  $(C_{12}H_9N_2O)_x$ , in which  $x$  is an even number—e.g., 4.

Properties of Emeraldine and Aniline Black.—Emeraldine † is produced by the limited oxidation of aniline or of aminodiphenylamine. It is also formed, as stated above, by the polymerisation of phenylquinonedi-imide. The free base forms a dark blue amorphous substance, which has the composition  $C_8H_5N$  (Nover) or  $C_{24}H_{20}N_4$  (Willstätter and Moore). It is insoluble in water, but dissolves in alcohol with a fine blue colour and in benzene with a red-violet colour. With concentrated sulphuric acid it gives a carmine-red solution, which yields a dark green precipitate of the sulphate on pouring into water. Other salts of emeraldine also show a green colour. By the action of reducing agents, emeraldine is converted into a leuco-base which reverts to emeraldine on exposure to the air. Heated with water in a sealed tube to  $150^\circ$  to  $160^\circ$  C., it is converted into Aniline black on the one hand and into its own leuco-base on the other (Willstätter and Moore). By the action of oxidising agents, emeraldine is converted into Aniline black.

Aniline black or nigraniline results from the direct oxidation of aniline, or of emeraldine, or of aminodiphenylamine. The free base is insoluble in water and either insoluble or sparingly soluble in all other solvents; it is slightly soluble in aniline with a violet colour, in phenol with a greenish-blue colour, and in nitrobenzene with a blue-violet colour. Concentrated sulphuric acid dissolves it with a violet colour, while fuming sulphuric acid yields various sulphonic acids. The salts of Aniline black are not stable and it is consequently difficult to obtain them of constant composition. Thus, the hydrochloride gradually loses hydrochloric acid on drying. Reducing agents convert Aniline black into an insoluble leuco-compound, which rapidly takes up oxygen from the air in presence of alkali with reformation of the black. When Aniline black is treated with bichromate it yields, according to Nietzki, ‡ a violet-black compound which contains chromic acid and which is not turned green by acids. Powerful oxidising agents, like chromic acid used in excess, convert Aniline black into quinone.

By the action of mild reducing agents, like sulphurous acid, ordinary Aniline black or nigraniline is converted into a green substance which is supposed to be identical with emeraldine. By further oxidation with bichromate of potash, manganese peroxide, bleaching powder, &c. nigraniline is converted into what is known as "ungreenable" Aniline black which is not affected by sulphurous acid. According to Liechti and Suida, § this product contains oxygen in the combined state, but otherwise it does not appear to have been exhaustively investigated. ||

Orthotoluidine, when treated like aniline, also yields a black which is very similar to Aniline black, from which it can, however, be distinguished by the

\* *Journ. Soc. Dyers and Col.*, 1908, p. 9.

† See also W. Nover, *Journ. Soc. Dyers and Col.*, 1907, p. 125.

‡ *Berl. Ber.*, 1879, p. 1094.

§ *Mith. d. techn. Geversmuseums in Wien*, 1884.

|| See Erban, *Journ. Soc. Dyers and Col.*, 1907, p. 17.



fact that the free base dissolves in chloroform with a blue-violet colour. Paratoluidine, on the other hand, does not appear to yield a black by oxidation (*Nietzki*).

*Application to Cotton.*—The methods and recipes for the dyeing of Aniline black on cotton are almost innumerable. In some of these the oxidising agent is first fixed on the cotton in an insoluble condition, and the dyeing is then effected in a bath containing aniline salt or by padding with a solution of the latter. Paraf\* suggested padding the goods in a solution of chromium chloride, and then passing through one of potassium chromate, when insoluble chromate of chromium is formed on the fibre. The goods are then dyed in a solution of aniline salt containing 2½ per cent. of a chlorate, after which they are taken out, wrung, and allowed to oxidise. Lauth† first dyes the cotton manganese bronze and then dyes in a bath containing 50 grms. aniline oil and 100 grms. hydrochloric acid per litre. The method can be simplified by first dyeing the cotton the required depth of shade of manganese bronze, then padding in a solution of aniline salt and leaving the goods batched over night. It is said that in this way an absolutely ungreenable black is obtained. Knecht‡ has recorded the observation that nitrated cotton padded with a solution of aniline salt and then allowed to age is dyed a full and fast shade of Aniline black. The observation is of some theoretical interest, but is of no practical value.

Attempts have also been made to fix the aniline on the fibre in an insoluble condition, previous to oxidising, but these have met with little or no success.

The only methods of dyeing Aniline black on cotton which have achieved practical success are those in which the aniline and the oxidising agent are both presented to the fibre in the soluble condition, the colouring matter forming more or less gradually and becoming fixed on the fibre as it forms. These may be conveniently classified under the following headings:—

- (1) Dyed blacks.
- (2) Aged blacks.‡
- (3) Steam blacks.

A dyed black is obtained by “dyeing” the cotton (*i.e.*, turning it in the manner employed for ordinary dyestuffs) in a solution containing aniline hydrochloride and a suitable oxidising agent. Bobœuf was the first to suggest the use of bichromates for this purpose, and the following process based on his discovery is given by Noeltzing and Lehne¶ for the dyeing of cotton yarn in the hank.

Two separate solutions are prepared—one with 6 kgs. (12 lbs.) of aniline, 9 kgs. (18 lbs.) of hydrochloric acid, and 12 kgs. (24 lbs.) of sulphuric acid in 200 litres (40 galls.) of water; the other with 12 kgs. (24 lbs.) of bichromate of soda in 200 litres (40 galls.) of water. After allowing to cool, equal volumes of either solution are poured into a small dish, and the yarn is rapidly passed through this bath in lots of 1 kg. (2 lbs.); within one or two minutes a bronze-black is developed. The material is then wrung out and steamed for 20 minutes at 3½ pounds pressure. The bronze-black becomes jet-

\* French Patent No. 71,692, 1866.

† French Patent No. 85,554, 1869.

‡ *Journ. Soc. Dyers and Col.*, 1898, p. 9.

§ The term “oxidation black” is frequently employed to designate an aged black. But since all Aniline blacks are produced by oxidation of aniline in presence of the fibre, the term cannot reasonably be used to distinguish between one method of oxidation and another.

¶ French Patent No. 68,079, 1865.

¶ *Anilinschwarz*, p. 54.

black, and is rendered practically ungreenable by the steaming. The hanks are finally washed and soaped at the boil. For the soaping a solution of 5 to 10 parts of oily soap per 1000 parts of water (with or without the addition of sodium carbonate) is used. The utility of the steaming is based on the fact that a black oxidised at an elevated temperature does not turn green so soon as those obtained at lower temperatures. Hydrochloric and sulphuric acid are used together to obtain a jet-black, since the former alone produces a bluish and the latter a reddish-black.

The two following processes give good results on cotton yarn. In both cases the amounts given relate to 100 lbs. cotton.

*Process A.*—The dye-bath is made up as follows:—

13 lbs. aniline salt.  
22 lbs. hydrochloric acid, 32° Tw.  
14 lbs. bichromate of soda.  
200 galls. water.

The aniline salt is first dissolved, then the hydrochloric acid is added, and lastly the cold solution of the bichromate. It is essential that the total volume of liquor should not exceed 200 galls.

The cotton yarn (which has been previously boiled in soda and washed) is turned in this bath for one hour cold, when the temperature is raised to 70° C. and the dyeing continued at this temperature for half an hour. It is then taken out, rinsed and soaped for half an hour at 60°, after which it may be impregnated with a weak solution of Turkey-red oil before being hydro-extracted and dried.

*Process B.*—The dye-bath is made up with:—

14 lbs. aniline salt.  
13 lbs. bichromate of soda.  
2 lbs. copper sulphate.  
2 galls. hydrochloric acid, 32° Tw.  
200 galls. water.

The hanks are turned in this for an hour and a half cold, and the temperature is raised to the boil in 45 minutes. The liquor is now run off and a fresh bath is got up with—

4 lbs. copperas.  
6 lbs. sulphuric acid.

The cotton is entered at 95°, turned ten minutes, then washed, soaped, and oiled. The object of the treatment with copperas is to deprive the black of the bronzy appearance which it acquires in the dye-bath.

It is possible to obtain a dyed black by the use of oxidising agents other than bichromate. Thus, Coquillion\* obtains a black by steeping the cotton for eight to twelve hours in a bath made up of aniline, hydrochloric acid, chlorate of potash, and chloride of iron, afterwards treating the black obtained with bichromate of potash, with the object of rendering it faster and preventing it from greening.

The ordinary dyed black on cotton yarn is not as well fixed as an aged black, and consequently it "rubs" badly, and has a rather dead appearance. On the other hand, a dyed black is not liable to tender the fibre to anything like the same extent as an aged black. The fastness of a dyed black to chlorine is said to be considerably increased by soaping, as well as by steaming.

**Aged Blacks.**—The principle adopted in the dyeing of aged blacks is to pad the cotton in a solution of aniline salt, an oxidising agent (chlorate of soda),

\* French Patent No. 106,031, 1875.

and a carrier of oxygen (e.g., a salt of copper, iron, vanadium, or a ferrocyanide), after which the fabric is aged either in an ageing-room or in a rapid ager, and is subsequently chromed. For cotton piece dyeing, aged blacks are technically far more important than either dyed or steam blacks.

In the provisional specification of Lightfoot's first patent,\* which is entitled "Improvements in Printing and Dyeing Textile Fabrics and Yarns," the following description is given:—

"I take 1 gallon of water, and dissolve in it 4 ozs. of chlorate of potash; to this I add aniline, or any of its analogues, by preference aniline, in the proportion of 8 ozs. per gallon, and an equal weight of hydrochloric acid. After stirring well, I add 1 pint of acetic acid per gallon and 8-oz. measure of perchloride of copper at 88° Tw., 4 ozs. salammoniac, or an equivalent quantity of other alkaline chloride. I steep the fabric or yarn in this solution, wring out, and dry, age two nights, and pass through a weak solution of alkali or soap, or, by preference, diluted hypochlorite of lime. An intense black is thus produced."

In the complete specification further particulars are given regarding the ageing and raising of the colour. After the words "wring out and dry," Lightfoot continues, "then I expose the goods in a room at from 60° to 70° F. for two or three days; the goods are now passed through water alone, or a solution containing alkaline or metallic salts (which develop the black much sooner and better). The alkalies and alkaline earths may be used for raising the black, such as caustic soda, caustic potash, caustic ammonia, caustic lime in solution in water; or the goods may be passed, after 'printing' and 'dyeing,' through a box containing rollers supplied with 'ammoniacal gas' (which I prefer when the black is printed along with 'steam colours' prior to steaming the goods). When the black is printed along with 'madder' or 'garancine' colours, they are aged or exposed in a room at from 60° to 70° F. for three days, and duned, dyed, washed, and passed through a solution of soap or dilute hypochlorite of lime, whereby an intense black is produced."

The full text of these portions of Lightfoot's patent for the production of a copper black in dyeing is given here because it forms the basis of the most important process of dyeing Aniline black at present in use. The proportions of the essential ingredients have been modified, pure aniline oil (or salt) has taken the place of the crude product which Lightfoot had at his disposal, chlorate of soda has taken the place of chlorate of potash (being cheaper and more readily soluble), while copper sulphate has been generally substituted for the chloride. In piece dyeing the slow and somewhat uncertain process of ageing in a room has been replaced by ageing in a rapid ager, and, in place of alkalies or bleaching powder, bichromate is in general use for "raising" or developing the black.

The composition of the Aniline black liquor and the conditions of working vary in different works, but the following black on pieces, which is given by K. Oehler, may be taken as representing a good average process.

The pieces are padded at full width with two or three nips in an Aniline black liquor made up as follows:—

- 120 lbs. (60 kilos.) aniline salt dissolved in 26 galls. 2 pints (320 litres) water.
  - 37 lbs. 9 ozs. (18 8 kilos.) sodium chlorate dissolved in 7 galls. 3 pints (37 litres) water.
  - 5½ lbs. (2.75 kilos.) copper sulphate dissolved in 10 galls. (50 litres) water.
  - 4 lbs. (2 kilos.) ammonium chloride dissolved in 2 galls. 3 pints (10 litres) water.
- To this add
- 4 galls. 3 pints (20 litres) aluminium acetate 15° Tw.

---

\* English Patent No. 151, 1863.

These solutions, prepared separately, and cooled, are mixed in a vat, and are made up to 100 gallons of liquor, which should stand at 12° Tw.

Another black, in which both copper and iron salts are used, while toluidine partly takes the place of aniline, is recommended by the Hoechst Farbwerke. Two standard solutions are prepared as follows:—

*Standard A.*

55 litres water.  
4,500 grms. aniline salt.  
1,350 „ toluidine.  
1,850 „ chlorate of soda.

*Standard B.*

1,850 grms. nitrate of iron.  
6 litres water.  
2,700 grms. copper sulphate solution (200 grms. per litre).

For use 8 litres of Standard A are mixed with 1 litre of Standard B.

After padding, the goods, which should contain their own weight of liquor, are dried and aged to develop the black. The drying, which constitutes one of the most important operations in the dyeing of an aged black, may be effected in various ways. Formerly this was done in an ageing-room, but, in consequence of the time required, the output is considerably curtailed. Drying on steam cylinders is accompanied by a certain amount of risk, since tendering may take place at the temperature of the cylinders, and is certain to result if the pieces become quite dry before leaving the machine. The ageing is then done in a machine like that shown in Fig. 65 at a temperature of about 45° C. In some machines the drying on cylinders and the ageing are conducted in the same chamber.

For continuous black dyeing, drying and ageing may also be effected together in an ager like that of C. A. Preibisch, shown in Fig. 64a.

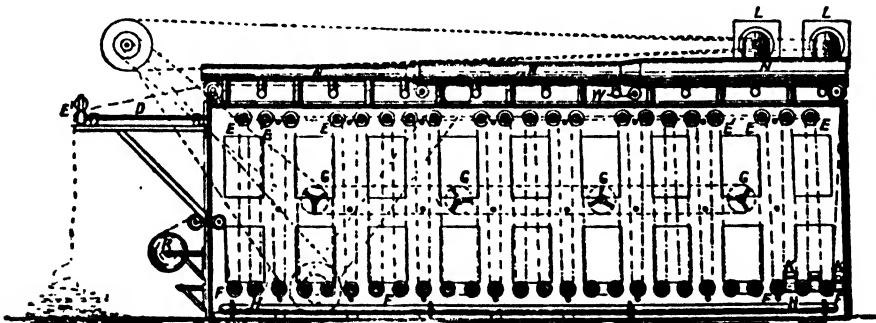


Fig. 64a.—Continuous ager for Aniline black.

The machine consists essentially of a chamber constructed of wood on an iron framework. The pieces pass in from the batch roller, R, through a slit in the end of the chamber, through which they are guided up and down by the slack rollers F, and the rollers E, which latter are geared to the shaft, D. On leaving the chamber at the end opposite to that at which they entered, the pieces are drawn by tension rollers, E', and plaited down. The heating of the chamber is effected by means of steam-pipes, H, at the bottom, and ventilation is effected by means of the fans, L, which are connected with the ventilating pipes, N, the air, which should have a temperature of 25° C., being admitted through openings (not shown in the figure) in the floor of the chamber. Fans, G, are provided at regular intervals in the interior of the chamber in order to effect a more even distribution of the incoming air. The temperature in the

chamber is maintained at 44° to 50° C. When the pieces have traversed about two-thirds of their path through the ager they are dry, and the formation of the black has begun. Since, however, a good black can only be obtained in presence of moisture, vessels, K, containing water are provided at the end of the chamber to supply the necessary degree of moisture.

After ageing, the goods should be of a dark green or almost black colour. They are next chromed (without intermediate washing) at 70° C. in a solution containing 3 grms. bichromate of soda and  $\frac{1}{4}$  gm. sulphuric acid per litre, after which they are soaped hot in a solution containing 3 grms. olive oil soap per litre, rinsed, and dried.

For mercerised goods, the strength of the Aniline black liquor can be diminished from 20 to 25 per cent.

The same black is applicable to cotton yarn (Diamond black). The hanks are first boiled in soda, rinsed well, and hydro-extracted. They are then turned in the liquor for half an hour, wrung lightly, and hydro-extracted so as to retain about their own weight of liquor. They are then well stretched, suspended (not too close together) on wooden sticks, and aged in a well ventilated and spacious drying room, the walls of which (in order to secure a uniform temperature in every part of the ager) are lined with wood. The temperature of the ager should be kept at 35° C. While in the ageing-room, the hanks are turned every two hours.

Hanks may also be aged on a machine similar in construction to Haubold's centrifugal drying machine (see *Drying Machinery*).

The ageing lasts from six to eight hours according to circumstances, and the yarn will be found to have assumed a green-black colour. It is now taken out and chromed, rinsed, and soaped as in the case of piece-goods. In chroming, it is turned rapidly for ten to fifteen minutes, and the subsequent soaping is continued for about fifteen minutes.

Since the yarn is wetted out previous to being immersed in the Aniline black liquor, the latter will naturally become diluted on treating successive lots of cotton. The liquor used for freshening up the bath must, consequently, be made stronger than the original liquor, the same proportions, however, being adhered to. The bath should always stand at 12° Tw.

The following is another recipe for an aged Aniline black on cotton yarn, in which the padding liquor is rendered viscous by the addition of starch, so as to bring about its more even distribution throughout the mass of the cotton on drying:—

A. 3 kilos. aniline oil are mixed with 3 kilos. hydrochloric acid of 34° Tw.

B. 1.5 kilos. copper sulphate, 1.4 kilos. salammoniac, and 1.2 kilos. potassium chlorate are dissolved together in water.

C. 0.4 kilo. starch is boiled up with water and diluted.

After cooling, A is stirred into B, and C is then added. The liquor is made up to 50 litres in case dry cotton is to be dyed, but if the cotton has previously been wetted out, the total volume should not exceed 40 litres. For the first kilo. of yarn use 5 litres of liquor and 1 litre of water. For further lots replenish with liquor only. The yarn is turned in this liquor, wrung, and aged at 30° C. It is then chromed, washed, and soaped hot. The higher the temperature in chroming the redder the shade of the black.

As with every other impregnation colour (as distinct from dyed colours), it is important that the cotton impregnated with the black liquor should not be allowed, previous to or during ageing, to come into contact with water; a single drop of water falling on to a piece will leave a grey spot. If any alkali comes into contact with the goods previous to ageing, the Aniline black will not develop at all in the contaminated parts and white spots or marks will result.

**Vanadium Black.**—Lightfoot\* first drew attention to the fact that of all the metallic compounds, those of vanadium were the most efficient in bringing about the formation of Aniline black from aniline salt and chlorate of potash, and his observation led to the adoption of salts of vanadium as carriers of oxygen in Aniline black dyeing. According to Guyard† and to Witz,‡ the amount of this metal required to bring about the formation of the black is exceedingly small. In printing, the latter used only 0·0012 grm. vanadium per litre of colour containing 80 grms. aniline salt. A black of the kind may be made up as follows:—

90 grms. aniline salt.  
20 grms. aniline oil.  
40 grms. sodium chlorate.  
5 c.c. vanadium chloride solution 1:100.  
845 c.c. water.

Pad, dry, age, chrome, wash, and soap.

*Vanadium Chloride Solution.*

10 grms. ammonium vanadate.  
70 grms. hydrochloric acid (30° Tw.).  
40 c.c. water.  
7 grms. glycerine.

Make up to one litre and heat until the solution has become blue.

Vanadium black is very seldom used in cotton dyeing on account of its great liability to produce tendering of the fibre. It is used for certain styles in calico-printing.

**Steam Black.**—In the latter part of his first patent specification relating to Aniline black, Lightfoot says:—

“And although I have described the use of the metallic salts of copper as used with aniline, I find that these salts may be replaced with some advantages by the use of the salt known as red prussiate of potash; and when this salt is used, it is used in substitution of other metallic salts, and I use it in the proportion of 4 to 6 ozs. red prussiate of potash to 1 lb. of a salt of aniline, or mixtures of aniline and its analogues, contained in 1 gallon of water. When red prussiate of potash is used, I also add to each gallon of colour 2 ozs. of oxalic acid, or other suitable acid, by preference oxalic acid. The material to be dyed or printed must be first aged, and afterwards steamed thirty to fifty minutes in the ordinary manner of steaming.”

This black is still produced by the method outlined by Lightfoot, with this difference that the expensive red prussiate is replaced by a mixture of yellow prussiate and chlorate of soda. The following may serve as an example of a steam black. The pieces are run through the following padding liquor:—

75 grms. aniline salt.  
35 grms. sodium chlorate.  
40 grms. yellow prussiate of potash  
Made up with water to 1,000 c.c.,

after which they are dried, steamed three minutes in a rapid ager, chromed, washed, and soaped.

The rapid ager consists of a spacious chamber, which is fitted with a number of copper rollers to guide the pieces while passing through the chamber. In the drawing the wall is cut out on one side to show the arrangement of the rollers. The pieces pass into the upper part through a small slit, and come out through the same opening after having been run through the whole

\* *Bull. Soc. Ind. de Mulhouse*, 1871, p. 235.

† *Bull. Soc. Chim. de Paris*, 1876, p. 58.

‡ *Bull. Soc. Ind. de Rouen*, 1876, p. 310.

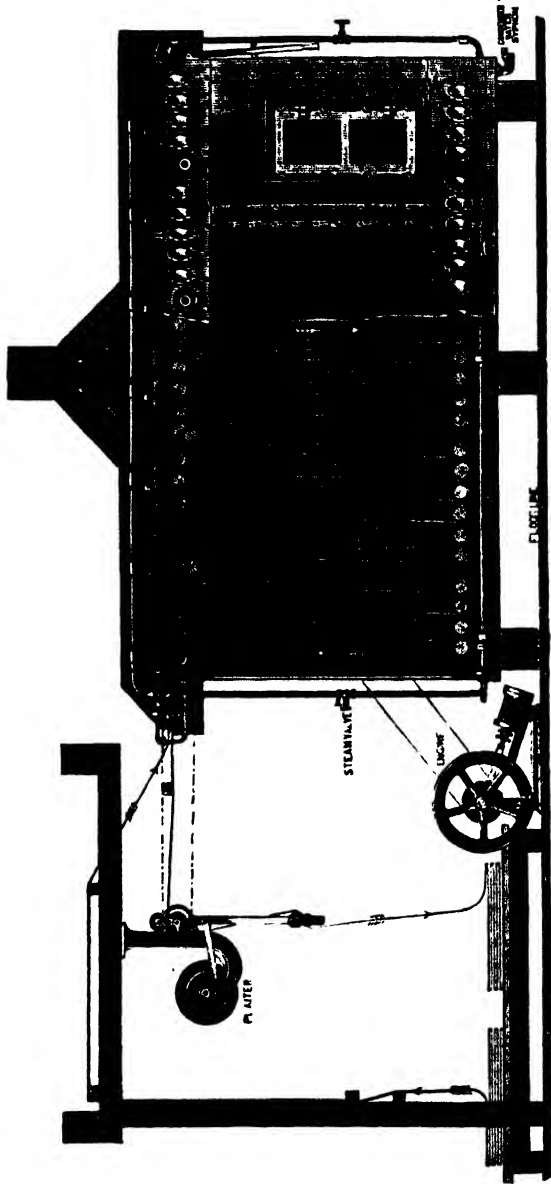


Fig. 65.—Rapid sger (Mather & Platt).

apparatus. Two copper tubes are fitted near the opening, and heated by steam to prevent the water from condensing; for the same purpose the cast-iron roof is constructed hollow, and heated by steam. The steam which has been used to heat the roof and copper pipes serves for supplying the interior with steam; if necessary, steam can be directly injected by means of a perforated pipe which is fixed on the bottom of the chamber. The temperature and the degree of moisture are shown by wet and dry bulb thermometers, which are placed in the chamber behind a glass plate.

Two large doors in the side of the machine afford convenient admission to the interior for "threading up" or other purposes. In an apparatus of medium size, the ageing of Aniline blacks is performed at the rate of about 60 yards per minute.

A steam Aniline black is not so liable to tender cotton as an aged black, but is more expensive.

**Aniline Black Produced by Air Oxidation.**—Recently A. G. Green has patented a process for the dyeing of Aniline black,\* the most remarkable feature of which is the absence in the padding liquor of any oxidising agent. In this process a small proportion of a paradiamine or of a para-amidophenol is added to the padding liquor, and this addition brings about the formation of the black by air oxidation in the ageing process. The following is one of the examples given in the English patent specification:—The padding mixture is prepared by adding a solution containing 48 pts. cupric chloride, 140 pts. ammonium chloride, and 14 pts. sodium metabisulphite in 500 pts. cold water to a solution composed of 50 pts. aniline, 2 pts. para-phenylenediamine, 15 pts. hydrochloric acid (30 per cent.), and 15 pts. formic acid in 1,500 pts. cold water.

In order to prevent the premature formation of oxidation products in the padding mixture, it has been found preferable to use the copper in the form of a cuprous salt, and the object of adding bisulphite is to reduce the cupric chloride to cuprous chloride. The object of adding such a large proportion of ammonium chloride is to keep the cuprous chloride in solution.

After padding, the goods are aged, chromed, &c. The advantages claimed for this new black are, in the first place, absence of tendering and, secondly, cheapness, inasmuch as a black can be obtained with 3 per cent. of aniline, while the output is greater than with an ordinary aged black.

When properly dyed on cotton, Aniline black is one of the finest and fastest blacks procurable. It is not changed by the action of light, acids, or alkalis, or any other influences which cotton goods are exposed to. The production of an entirely satisfactory Aniline black is, however, not a simple matter, and requires experience, skill, and careful supervision.

Unevenness in Aniline blacks may result from the usual causes which bring about this fault in other colours, and which need not be specially enumerated here. Aged or steam blacks, if unevenly impregnated, or if allowed to come into contact with water (even wet hands) before the formation of the black has taken place, will turn out faulty.

The greening of Aniline blacks which was frequently so great a source of trouble is due to insufficient oxidation. Goods which show this fault usually leave the hands of the dyer in an apparently faultless condition, but on storing, especially in localities where there may be sulphur dioxide (where gas is burnt), or sulphuretted hydrogen in the atmosphere, they assume after a time a dark green colour. The addition of a small proportion of paraphenylenediamine to the padding liquor (for an aged black) has been suggested as a means of preventing or diminishing the tendency to "green," but the plan now

\* *Journ. Soc. Dyers and Col.*, 1908, p. 231.



more generally adopted is to treat the black after ageing with an oxidising agent (usually bichromate alone or in conjunction with sulphuric acid) at a sufficiently high temperature.

To test whether an Aniline black is liable to "green," a sample of the dyed material is warmed with a fairly strong solution of bisulphite of soda, washed and dried. If it remains unchanged, the black will not turn green on exposure.

The tendency of Aniline black to "rub" is only met with in dyed blacks. By suitable manipulation in the dyeing, this tendency can be considerably diminished, but can never be entirely got rid of. When such goods are heavily starched they do not rub.

Sometimes Aniline blacks are liable to turn out bronzy, and this fault is said to be due to over-oxidation. It can usually be rectified by treating the goods with an acid solution of a reducing agent, such as titanous chloride, or, in some cases, copperas.

The tendering of cotton-dyed Aniline black is perhaps the commonest of all faults. Some ascribe this to the production of oxycellulose, but no direct proof has ever been advanced that this is really the cause. Although the cotton is undoubtedly brought into contact with strong oxidising agents in the process, it must be borne in mind that aniline is a fairly strong reducing agent, and it is, therefore, likely that even if the oxidising action should become energetic (as is sometimes the case in steaming or even previous to steaming), the aniline or even the Aniline black will be attacked before the cotton. The composition of the hydrochloride of Aniline black is still uncertain, this being due to its tendency to decompose on drying. But whereas aniline salt contains over 28 per cent. of hydrochloric acid, and the Aniline black which results from its oxidation contains certainly not more than 14 per cent., it is clear that during the formation of the black a considerable amount of free hydrochloric acid must be formed, which, acting on the cellulose at the elevated temperature of the ager (or for a prolonged period in ageing in a room) is likely to attack the cotton and produce tendering by the formation of hydrocellulose. It was evidently with the object of minimising this action that Lightfoot added ammonium chloride, "or an equivalent quantity of other alkaline chloride," to his padding liquor.

It has been suggested to replace the hydrochloric acid by other acids which have less tendency to attack cellulose, such as hydrofluoric acid, tartaric and formic acids, but any advantage gained by their use is more than counterbalanced by inferiority of the resulting colour. The degree of tendering varies according to the kind of black used. Thus, a dyed black scarcely affects the tensile strength of the cotton, while of the blacks produced by padding, the steam black is least liable to tender. In the case of the dyed black this may be explained by the fact that even if the dye-bath is used hot, the acid with which the fibre is in contact is only very dilute, while in the case of steam black, any hydrochloric acid liberated is largely, if not entirely, neutralised by the yellow prussiate present. In the case of aged blacks it is impossible to absolutely prevent tendering, though in the case of the copper-black dyers have now succeeded in reducing the tendering below 10 per cent.

**Bottomed and Topped Blacks.**—At one time it was a common practice to bottom the cotton with an ordinary direct blue or black previous to dyeing an aged black (Swiss black). Dyed Aniline black is even now frequently produced on a bottom of direct cotton black, for the purpose of diminishing the tendency to rubbing by decreasing the quantity of Aniline black. The cotton is dyed with a direct cotton black, say, 3 to 4 per cent. Columbia black FF or Diamineral black B, and, after rinsing, worked in a short bath with 4 per cent. aniline salt, 6 to 7 per cent. hydrochloric acid (32° Tw.), and 3 per cent. sul-

phuric acid, to which, immediately before use, 3 per cent. copper sulphate and 4 per cent. sodium bichromate are added. Work one to one and a-half hours cold, heat within half an hour to 50° to 60° C., rinse well, and soap hot. Congo red and Benzopurpurin 4 B have been used in the same way before the introduction of direct cotton blacks.

Kertess has suggested the use for a similar purpose of Diamine black R O or B H, which is first dyed in the ordinary way, then diazotised and developed in metatolylenediamine. The cotton is then impregnated with copper Aniline black liquor at 4° Tw., when it is aged, chromed, &c., as usual. In consequence of these additional operations, the cost of the black, in spite of whatever saving there is in aniline salt, &c., is materially increased.

Every Aniline black that has been chromed is at the same time mordanted with chromium, so that it is rational to dye it in any mordant colour either for intensifying or modifying the shade. At one time when aniline was still an expensive article of commerce, logwood was commonly used for the purpose of filling up the black, and this practice is continued at the present time.

*Application to Wool.*—For ordinary wool Aniline black has little or no affinity, but if, according to Lightfoot,\* the fibre is first chlorinated (see *Wool*), it can be dyed like cotton. Lightfoot assumed that ordinary wool could not be dyed on account of the reducing (deoxidising) action of the fibre, but Bethmann † ascribes this property to the basic character of the wool fibre. His process of rendering wool capable of being dyed Aniline black consists essentially in treating the fibre with a mineral acid—*e.g.*, boiling for an hour with 5 per cent. sulphuric acid.

After being suitably prepared, wool can be dyed Aniline black by methods similar to those used for cotton. The colour is seldom applied on wool.

*Application to Silk.*—Unlike wool, silk can be dyed Aniline black without any previous preparation. Although no difficulty arises in applying Aniline black to silk, it is very seldom dyed on this fibre, except in cases where extreme fastness is a desideratum. For satins and other fabrics consisting of silk and cotton, the copper-black finds some application, especially for umbrella cloths.

Blacks produced from Bases other than Aniline.—According to Gilliard. P. Monnet et Cartier an ungreenable black can be produced with the aid of parphenylenediamine. They state that a mixture of equal molecules of parphenylenediamine and aniline produces a brownish-black, whereas a mixture of 1 molecule of parphenylenediamine with 2 or 3 molecules of aniline or toluidine yields good bluish-blacks, hence they mix the hydrochlorides of parphenylenediamine in the corresponding proportions, and use for 100 kgs. (lbs.) of cotton, 4 to 6 kgs. (lbs.) of this mixture, 3 kgs. (lbs.) of sodium chloride, and 40 grms. (about 1 oz.) of vanadium chloride; the bath is kept at 60° C., and thus a soluble dyestuff is formed. This is taken up by the fibre, and the bath becomes colourless.

**Diphenyl Black.**—This black, which was introduced by Meister Lucius & Brining, is produced on the fibre by the oxidation of para-aminodiphenylamine, or mixtures of this compound with aniline. For piece goods the following process is recommended by this firm:—

*Standard A.*

600 grms. gum tragacanth thickening (1 : 10) are diluted with  
750 c.c. water ;  
400 grms. diphenyl base are dissolved warm with  
500 „ lactic acid (50 per cent.) and  
1,300 „ acetic acid, stirred into the tragacanth thickening, and made up with  
1,450 c.c. water to 5 kilos.

\* English Patent No. 2327, 1865.

† *Journ. Soc. Dyers and Col.*, 1901, p. 204.

*Standard B.*

250 grms. aluminium chloride (53° Tw.).  
 250 „ chromium chloride (53° Tw.).  
 40 „ cupric chloride (77° Tw.).  
 3,460 c.c. water.  
 300 grms sodium chlorate dissolved in  
 600 c.c. hot water, and then add  
 100 grms. oil of turpentine.

These standards keep well without undergoing any deterioration. For use, add Standard B to an equal weight of Standard A. The pieces are padded in the liquor, dried slowly, steamed for two minutes in a rapid ager, and soaped without previous chroming, the effect of chroming on this black being such as to give it a brownish caste.

Diphenyl black is also suited for the dyeing of yarn. The black obtained is not inferior in appearance to an Aniline black, does not green, and does not tender the fibre. It is, however, more expensive than Aniline black.

The property of dyeing textile fibres when oxidised in their presence is not peculiar to aniline and the other bases named above, but is common to most of the amines of the aromatic series. Although various colours can be obtained in this way, they usually lack brilliancy, and as they can be obtained more conveniently or cheaper by other means, the method is seldom resorted to.

**Naphthylamine Violet.**—This colour may be produced on the fibre by the oxidation of alpha-naphthylamine, and was formerly used in calico-printing.

**Naphthylamine brown** is obtained by "dyeing" cotton which has been previously dyed manganese bronze with alpha-naphthylamine hydrochloride.

**PARAMINE BROWN (B.A.S.F.).**

A very good brown can be produced, according to H. Schmid,\* by oxidation of *p* phenylenediamine by a process analogous to that used for Aniline black.

Paraphenylenediamine is marketed for this purpose under the designation *Paramine* (B.A.S.F.).

The following formula is given for padding cotton cloth:—15 to 20 grms. *Paramine* (B.A.S.F.) are dissolved in 300 c.c. hot water, and diluted with 450 c.c. cold water; 1.5 grms. Rongalite C are dissolved in the solution, and there are added, successively, 15 to 20 grms. sodium chlorate dissolved in 50 c.c. water, 15 to 20 grms. ammonium chloride dissolved in 50 c.c. water, 15 grms. ammonium vanadate solution (1 : 1,000), and 30 to 40 grms. solution of tartar emetic in glycerine (prepared by dissolving 40 grms. tartar emetic in 620 c.c. warm water, and adding 340 grms. glycerine). The solution is diluted to one litre. After one hour it will be colourless. It will keep for about two days. Immediately before use it is sieved through cotton cloth. The pieces to be dyed are passed through the padding liquor, dried in the hot flue at 40° to 45° C., steamed for five minutes in the Mather-Platt ager, rinsed, and soaped. Instead of steaming, the pieces may be passed through a lukewarm solution of 2 to 3 grms. bichromate per litre. The tartar emetic is added for the purpose of delaying the oxidation for resist printing.

Recently a very pure *p* phenylenediamine has been furnished under the name *Paramine extra* (B.A.S.F.), which yields a more agreeable shade of brown. This may be used without tartar emetic—e.g., by the following formula:—12 to 16 grms. *Paramine extra*, 12 to 16 grms. sodium chlorate, 12 to 16 grms. ammonium chloride, and 0.015 gm. ammonium vanadate in 1 litre.

\* H. Schmid, English Patent 17,241 of 1906 (B.A.S.F.), *Journ. Soc. Dyers and Col.*, 1906, pp. 123 and 205.

Paramine brown dyes a yellowish-brown which possesses very good fastness to light and washing, and is moderately fast to chlorine.

M. Lummersheim \* has patented a process of shading Paramine brown by diazotising and developing with resorcin, naphthol, &c., or by coupling with diazotised paranitraniline on the fibre.

Paramine brown may also be produced on wool and silk, and when dyed on a bottom of Prussian blue it yields a black.†

**FUSCAMINE G** (B.A.S.F.), produced by the oxidation of *p* aminophenol in a similar manner as Paramine brown, dyes a more yellowish shade of brown.

#### ARTIFICIAL INDIGO (INDIGOTIN), $C_{16}H_{10}N_2O_2$ .

Indigo, natural and artificial, has been discussed in Part VI., and it need hardly be stated that the active constituents of both kinds are chemically identical. The differences observed in practice are caused by the differing physical condition, or by the impurities present in natural or artificial indigo. Of the latter the bacteria only are of some importance, as they are generated during the manufacturing process, and assist in setting up a fermentation or woad vat. These bacteria are also met with in vats prepared with artificial indigo, as quantities occur in the air and in the woad employed. Since, however, they are more abundant in natural indigo, the vats prepared with the latter develop them more rapidly. In order to counteract this drawback, it is sufficient to add a small quantity of natural indigo, or, just as well, a few pails of a well-set vat prepared with either natural or artificial indigo, when setting a new vat. As the bacteria generate acid which is to be neutralised by lime, a rapidly developing vat with natural indigo will require more lime than a slowly fermenting vat with artificial indigo. These differences will disappear after a few days' working. The solubility of the artificial product has been very much improved, and the various brands of Indigo (M.L.B.) and the S brands of Indigo pure (B.A.S.F.) are very suitable for all vats, the fermentation vats included. The powder brands are best wetted in hot water, either by placing them in a weighted bag, or by placing them on sackcloth spread over a barrel half filled with strongly boiling water, and covering the indigo with sackcloth. The steam passing through will moisten the powder.

INDIGO VAT and INDIGO SOLUTION (B.A.S.F. and M.L.B.) contain indigotin in the reduced state, and do not require previous reducing by the dyer, but may be added direct to any kind of vat, thus saving time and labour. This advantage is considerable with the woad vat, which can be fed during the day's working with fresh quantities of indigo vat, thus enabling a greater number of lots to be dyed without waiting for the reduction of the indigo added.

Since strong alkalinity prevents the proper fermentation in the woad vat, the latter will rarely be too alkaline. The hydrosulphite vat, however, unless prepared with care may easily become so strongly alkaline as to be detrimental to the wool to be dyed. Hence, the makers of artificial indigo have endeavoured to avoid altogether the presence of any fixed caustic alkali. This is attained by the use of *Indigo vat* (reduced indigo) and hydrosulphite in powder (or in solution free from caustic soda), the necessary alkalinity being produced by the addition of ammonia. Since, however, ammonia does not readily dissolve indigo and the hydrosulphite fairly rapidly develops acid by the action of the air, the indigo white might be precipitated. In order to prevent this, some glue is added which keeps the indigo white in solution.‡

\* *Journ. Soc. Dyers and Col.*, 1908, p. 52.

† C. Ekstein, *Journ. Soc. Dyers and Col.*, 1908, p. 234.

‡ English Patent 7829 1900 (M.L.R.). English Patent 8510, 1902 (B.A.S.F.).

In addition to pure indigotin which is marketed as *Indigo pure* (B.A.S.F.) and *Indigo* (M.L.B.) some other brands are furnished to the trade as INDIGO R and R R (M.L.B.); INDIGO T (M.L.B.); INDIGO PURE R (B.A.S.F.); INDIGO PURE G (B.A.S.F.) (*Mono- and di-bromo-indigotin*; *tolyl-indigotin*).

These brands closely resemble indigo and are applied in much the same way, best in the hydrosulphite vat, but also in the fermentation vat. They are readily reduced by hydrosulphite, but their leuco-compounds are slightly less soluble in alkali. *Indigo R* and *RR* dye brighter and redder shades of blue than ordinary indigo, and are very valuable for shading the same. *Indigo G* and *T* dye more greenish blues which also may be used for shading ordinary indigo. The fastness of these brands is equal, or even greater than, that of ordinary indigo, especially the fastness to chlorine. They withstand oxidising agents better and, therefore, they are less easily discharged by the chromate or chlorate discharges.

INDIGO PURE RBN (B.A.S.F.) is a bromine derivative of indigo recently brought into the market, which gives pure blue shades, brighter and greener than ordinary indigo of very good fastness to light, washing, milling, alkalies, acids, &c. This brand resembles the *Ciba blues* described hereafter.

INDIGOTIN 4 B (M.L.B.), a very recently issued brand, also produces very pure shades of blue.

BROMINE INDIGO FB (Bayer) is also a very recent product resembling the last named brand and the *Ciba blues*, producing a bright indigo blue of good fastness; the fastness to light, however, is not quite as good, the colour becoming much greener on exposure to light.

CIBA BLUE B and BB (Ch. Ind. Basle).

The *Ciba blues* are tri- and tetra-bromo-indigotin, produced by the action of bromine on indigo in a hot solution of nitrobenzene. These dyestuffs are distinguished by their beautiful blue shades which are purer and greener than those of indigo and equal or even better in fastness. In their general behaviour they closely resemble ordinary indigo, and are dyed in the same kinds of vat, principally in the hydrosulphite vat. They show, however, more affinity to the vegetable fibre, the bath being much better exhausted than in the case of indigo.

The *Ciba blues* are applicable for dyeing the vegetable and the animal fibres, and can be combined well with the other commercial vat-dyes. They may be used in various ways for printing and discharging purposes, being well discharged by means of chlorate.

*Ciba blue* is marketed as a blue powder or paste insoluble in water and in dilute acids or alkalies. The solution in concentrated sulphuric acid is blue, and on diluting it yields a blue precipitate.

*Application.*—For dissolving the *Ciba blues* it is necessary, for medium shades on cotton, to use  $3\frac{1}{2}$  times their weight of caustic soda lye (75° Tw.) and also  $3\frac{1}{2}$  times the quantity of sodium hydrosulphite in powder (80 to 85 per cent.), reckoned on the weight of dyestuff. For light shades the quantities of hydrosulphite and caustic soda are increased to five to six times the quantity of dyestuff, for dark shades these proportions are diminished to only twice as much. In wool dyeing,  $2\frac{1}{2}$  times the quantity of caustic soda and hydrosulphite in powder are sufficient. For instance, a paste is made up of 1 part of dyestuff with  $1\frac{1}{2}$  parts caustic soda lye and hot water; the remaining half of caustic soda ( $1\frac{1}{4}$  parts) is added to 15 times as much cold water, whereupon  $3\frac{1}{2}$  parts sodium hydrosulphite in powder are gradually added whilst slowly stirring. Hot water is then added and the solution completed by gentle boiling. The solution is passed through a fine sieve into the dye-bath heated to 60° to 70° C.

It is especially necessary to take care that the reduced dye solution as well as the dye-bath be of a golden-yellow tinge; greenish looking baths are not in a proper condition, and in consequence give dull and uneven dyeings. Such baths, in most cases, may be corrected by adding caustic soda.

Cotton is dyed at 60° to 70° C., or in the case of goods which are difficult to penetrate the temperature is raised to 70° to 80° C. In order to facilitate the penetration of the goods it is recommended to make an addition of 1½ kgs. per 1,000 litres (½ lb. per 100 galls.) of Turkey-red oil. The well wetted material is worked in the bath containing the necessary quantity of dyestuff for about half an hour, squeezed or wrung, exposed to the air, and well washed. Deep shades on yarn should be soaped hot with soap and soda for twenty to twenty-five minutes; the soaping is essential for the production of bright shades and considerably improves their fastness to washing and bleaching. By half an hour's after-treatment with 2 to 3 per cent. copper sulphate and 2 to 3 per cent. acetic acid at 90° C. a greener shade, possessing slightly superior fastness to chlorine, is obtained. Dark shades on pieces, after rinsing, are further developed by a treatment for twenty minutes at 70° C. with 3 per cent. bichromate and 1½ per cent. acetic acid.

The beautiful blue shades produced with Ciba blue are very fast to light, washing, alkalies, and acids; they withstand chlorine well, but not kier-boiling under pressure.

Wool.—The dyestuff dissolved with 2½ times the quantity of caustic soda (75° Tw.) and hydrosulphite in powder is passed through a sieve into the dye-liquor heated to 60° to 70° C., after which 1 to 3 parts sulphuric acid (1 : 10) per 1,000 parts are added in order to neutralise the bath. In so doing, particular care should be taken that the bath does not show the slightest acid reaction with litmus paper, and also remains yellow. Greenish-milky baths contain too much acid, and should be neutralised with caustic soda lye. The previously wetted wool is entered into the bath, dyed for fifteen to twenty minutes, squeezed, and exposed to the air for fifteen to twenty minutes. It is then well rinsed, developed at 30° to 40° C. in acidulated water (8 parts hydrochloric acid per 1,000 parts water), and again well rinsed. A beautiful blue is obtained of excellent fastness to light, washing, milling, potting, alkalies, acids, and stoving.

Silk can be dyed similarly to wool, and the shades obtained are remarkable for their brightness, as well as for possessing good fastness to light and water.

Half-silk is dyed like cotton.

**CIBA VIOLET B and R** (Ch. Ind. Basle).

The Ciba violets have recently appeared in the market, and are halogenated compounds of alpha-oxythionaphthene and a substituted isatine; it is, therefore, closely related to the indigo and thio-indigo series (see pp. 662 and 665).\* They resemble Ciba blue in tinctorial properties and fastness, and yield on the various fibres, when dyed in the vat, violets of very good fastness to light, washing, milling, alkalies, and acids.

**THIO-INDIGO RED B** (Kalle).†

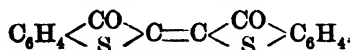
In addition to the halogen derivatives of indigo, described on the preceding pages, a sulphur compound, analogous to indigo, discovered in 1905 by Prof. P. Friedländer, of Vienna, has attracted the attention of chemists and dyers, this product being of great scientific interest and, owing to its unprecedented fastness, also of very considerable practical value. The discovery of thio-indigo may be regarded as one of the most important, if not the most important, in the chemistry of indigo since Heumann's synthesis which led to the successful manufacture of artificial indigo. By it a new field has been opened up

\* G. Engi, *Chemiker Zeitung*, 1908, p. 1179.

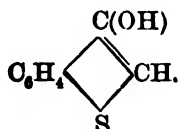
† *Journ. Soc. Dyers and Col.*, 1906, p. 156; 1907, p. 70.

which has already resulted in the discovery of various other colouring matters of the same class, and possibly may lead to the production of actual substitutes for Turkey red.

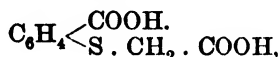
Thio-indigo red B is constituted according to the formula



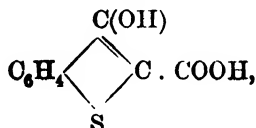
The scientific name *Thio-naphthens indigo* has been proposed for this compound. It is produced by the oxidation of *thio-indoxyl*—i.e., *alpha-oxythio-naphthens*—



The latter compound may be prepared in various ways, for instance, by boiling *phenylthio-glycol carboxylic acid*,



with alkalis, whereby ring formation readily ensues and *alpha-oxythio-naphthens carboxylic acid*,



results, which, when heated in an acid medium, loses  $\text{CO}_2$  with the formation of oxythio-naphthens or thio-indoxyl.

Thio-indigo red B forms red-brown crystals possessing a metallic reflex. The commercial product is a bluish-red powder, or a bluish-red paste containing 20 per cent. of the dyestuff. It is insoluble in water, dilute acids and alkalis, but soluble in many organic solvents, such as chloroform, ether, benzene, xylene, &c., yielding red solutions, which are characterised by their intense yellow fluorescence. It is also soluble in boiling alcohol, but without fluorescence; on cooling, it separates out. In concentrated sulphuric acid it dissolves with a bluish-green colour; on diluting, the dyestuff separates out completely. With fuming sulphuric acid a sulphonic acid is formed which, however, seems to be without technical value. Concentrated nitric acid is apparently without action in the cold, but when boiled with the dyestuff, oxidation takes place and a yellow solution results. If strong nitric acid be added to the solution of the dyestuff in ordinary strong sulphuric acid, an orange-coloured nitro-compound is probably formed.

One of the most characteristic properties of Thio-indigo red is its remarkable stability in presence of strong oxidising agents. Thus it is not affected by boiling with chromic acid, alkaline red prussiate, or bleaching powder. When cotton dyed with Thio-indigo red is boiled in a strong hypochlorite solution, the cotton may be completely destroyed, leaving the dyestuff unchanged as a red scum on the surface of the liquor.

By alkaline reducing agents, such as sodium hydrosulphite, copperas, or zinc and caustic soda, or glucose and caustic soda, Thio-indigo red is readily reduced and dissolved on warming, yielding the leuco-compound which forms a

clear yellow vat, from which the red is reproduced by exposure to air. The dyestuff is also completely reduced by boiling with sodium sulphide and caustic soda. The dyestuff is more readily affected by reducing agents than indigo, but less readily by oxidising agents. When cotton is bottomed with Thio-indigo red and then dyed in an indigo vat, containing a slight excess of hydrosulphite, practically all the red is stripped, and the cotton dyed an almost pure shade of indigo.

Like indigotin the new dyestuff readily sublimates on heating.

*Application.*—The application of Thio-indigo red in dyeing is exactly like that of indigo, hydrosulphite, copperas or zinc vats being used, and in addition, solutions prepared with sodium sulphide similarly to the sulphide colours. Any apparatus used for dyeing indigo can be employed for Thio-indigo red. The colour is also suitable for calico-printing, and for this purpose the makers recommend printing the colour thickened with British gum with the addition of caustic soda, and steaming in a rapid ager with steam as free from air as possible, and at a temperature above 100° C., or deeper shades with the addition of sodium sulphoxylate-formaldehyde (Hydrosulphite N F, Hyraldite or Rongalite, see p. 199).

Cotton is dyed in the vat (hydrosulphite, copperas, zinc dust, &c.), or from a sodium sulphide bath.

*Hydrosulphite Vat.*—The working of the vat is easier than in the case of indigo, as the thio-indigo not only oxidises less quickly in the bath, but is also more easily again reduced. In general, it can be said that Thio-indigo red requires about one-half the quantity of hydrosulphite for reduction as indigo. Stir 50 kgs. (lbs.) Thio-indigo red B paste with 200 litres (20 galls.) water, and add 150 litres (15 galls.) hydrosulphite of 25° Tw., or 1½ kgs. (lbs.) hydrosulphite in powder, heat to 35° to 40° C., and, after stirring for half an hour, add 10 litres (1 gall.) caustic soda lye of 75° Tw., or 15 kgs. (lbs.) soda ash dissolved in 100 litres (10 galls.) water. Stir until the reduction is complete—i.e., until the colouring matter has given a yellow solution—then dilute with water and make up to 1,000 litres (100 galls.). After twelve hours the clear liquor, if not immediately used, should be stored in carboys or casks. This solution is used as a stock-vat. For dyeing, run into a vat of 1,000 litres (220 galls.) capacity about 800 litres (175 galls.) water of a temperature of about 20° to 24° C., add 3 to 5 litres (1 gall.) hydrosulphite 25° Tw., in order to prevent oxidation by the oxygen contained in the water, stir and add 200 litres (44 galls.) from the stock-vat. Then stir gently, allow to stand for half an hour and start the dyeing operation. For obtaining full shades, it is advisable to use a more concentrated bath containing about 15 to 20 grms. Thio-indigo red B paste per litre (1½ to 2 lbs. per 10 galls.), a dip from three to eight minutes duration being recommended. When dyeing continuously, the bath is freshened up with corresponding quantities of stock liquor, hydrosulphite being added from time to time in order to maintain the dye-vat in the proper condition.

The hydrosulphite vat is the cleanest and easiest to work, and when dyeing in machines, or for piece goods in the continuous vat, is almost the only one worthy of consideration.

*Copperas Vat.*—Stir 50 kgs. (lbs.) Thio-indigo red paste with 200 litres (20 galls.) water, and add 50 kgs. (lbs.) copperas dissolved in 200 litres (20 galls.) water, then add 300 kgs. (lbs.) milk of lime 20 per cent., and 200 litres (20 galls.) water. Stir until the dyestuff is reduced, forming a yellow-coloured solution. One thus obtains a stock vat which is employed in practically the same way as the hydrosulphite stock vat.

*Sodium Sulphide Bath.*—Sodium sulphide reduces Thio-indigo red to its leuco-compound and thus forms a vat in which cotton may be dyed in a similar



manner as with the ordinary sulphide colours (p. 447). The duration of the dyeing operation is, however, considerably shorter, and it is advantageously carried out in a cold or lukewarm bath. 1 kg. (lb.) of the paste is heated with a solution of 300 grms. (5 oz.) sodium sulphide in 1 litre (pint) water for five to ten minutes to 60° C., when reduction and solution will have been effected. The dye-bath is made up with the requisite amount of this solution to give the required shade, along with 50 per cent. common salt and 10 per cent. soda ash. The bath should be kept concentrated (not to exceed 20 times the weight of the cotton), and an immersion of twenty minutes is sufficient to obtain the maximum depth.

Thio-indigo red can be dyed in conjunction with all known sulphide colours. For light shading the mixed colours can be dyed in one bath, the goods are then squeezed or wrung off, opened out, and finally rinsed. For heavier shading the goods previously dyed with a sulphide colour are topped with Thio-indigo red in a cold bath. Other colouring matters which are not sensitive to sodium sulphide, such as indigo, Indanthrene, Primuline, &c., can also be topped in a similar manner.

Perfectly level colours, from a delicate pink to a deep bluish-red are obtained with Thio-indigo red which are extremely fast to all agents. Of special importance is their unequalled fastness to light and oxidising agents (chloride of lime, hydrogen peroxide, &c.).

Wool can be dyed with Thio-indigo red in a fermentation or in a hydrosulphite bath, as also in a sodium sulphide bath. The leuco-compound oxidises on the fibre more slowly than leuco-indigo, and, as a result, level colours are very easily obtained both in dark and in light shades.

*Hydrosulphite Vat.*—The stock solution is prepared as described for cotton. For delicate pinks vats containing 2 to 3 kgs. (lbs.) Thio-indigo red B in paste per 1,000 litres (100 galls.); for deeper shades 5 kgs. (lbs.) for the same volume of liquor are prepared. The dye-bath is heated to 60° C., and some hydrosulphite is added before the stock solution. A certain percentage of alkali is requisite in the dye-bath, which, if too high, attacks the wool fibre, and if too low, the shade of the dyeing obtained turns out dull and bluish. The experienced dyer will easily ascertain whether the vat has the right proportions by rubbing his fingers, wetted with the vat liquor, against each other. The titrimetric test, however, is more reliable. A measured quantity of the vat liquor should require about one-tenth of its volume of sulphuric acid (1 : 100) to render it neutral—i.e., 100 c.c. vat liquor should require 10 c.c. sulphuric acid (1 : 100) for neutralising. When less sulphuric acid is wanted, then there is a deficiency of caustic soda; if more acid is required, the excess of caustic soda must be partially neutralised by addition of sodium bisulphite. If the vat shows a good bloom, and contains the right percentage of alkali, enter the moistened wool at 60° C., work in the same manner as in the ordinary vat ten to thirty minutes, lift, and squeeze off. Thio-indigo oxidises on the fibre more slowly than indigo, consequently the colours turn out more uniform than those obtained with indigo. To maintain the vat in the right condition the necessary quantities of stock solution, hydrosulphite, bisulphite, or caustic soda are added.

Owing to the fact that indigo requires a much larger quantity of hydrosulphite for its reduction than Thio-indigo red, it is preferable for obtaining heavy shades, such as deep violets or the reddening of deep blues, to dye from separate vats, first with indigo, and subsequently with Thio-indigo red; no appreciable proportion of indigo will be stripped. However, to completely overcome this danger, one can top the wool previously dyed with indigo with Thio-indigo red from a sodium sulphide bath. Light shades, such as delicate pearl or heliotrope, are best obtained by dyeing the mixed indigoes in one vat.

A stock liquor prepared with Thio-indigo red B and sodium sulphide may be mixed without disadvantage with an indigo hydrosulphite liquor.

*Sodium Sulphide Bath.*—The bath is prepared as described for cotton, and titrated for alkalinity as stated in the case of the hydrosulphite bath for wool. In this case, however, 100 c.c. of the dye-liquor should require 6 to 8 c.c. of sulphuric acid (1 : 100) to render it neutral. If less sulphuric is used, the bath being otherwise in good condition, it may be used; if, however, more than 8 c.c. acid are required for neutralisation, the proper degree of alkalinity should be produced by adding sodium bisulphite. In titrating, litmus paper is used as an indicator. The method of dyeing wool is the same as when dyeing in the hydrosulphite vat.

The colours obtained, whether in the hydrosulphite or sulphide vat, are equally as fast to washing, soaping, milling, stoving, steaming, alkalis, acids, and cross-dyeing. The fastness is superior to that of indigo. The fastness to light and weathering far exceeds that of all the hitherto known red colouring matters. The extraordinary fastness of Thio-indigo red to oxidising agents renders it, even in the lightest shades, specially suitable for topping with fast mordant colours, either with previous mordanting, or by dyeing and subsequent chroming.

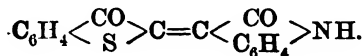
Silk can be dyed like wool from a hydrosulphite bath, similar results being obtained. Silk weighted with tin is also capable of being dyed in the same manner.

Mixed fabrics can also be dyed, and, as of the first importance, gloria (wool and silk) comes into consideration. For the production of pinks and reds upon fabrics used for sunshade coverings, trimmings, &c., where a considerable resistance to light and atmospheric influences is desired, Thio-indigo red is specially to be recommended.

Reactions on the Fibre.—Indigo-dyed goods which have been reddened by the addition of Thio-indigo red will not give the same nitric acid test as those dyed with indigo alone. Thio-indigo red being practically unaffected by nitric acid, there will be produced an orange to a scarlet spot. This change should be taken into consideration, the goods being not inferior in value, but considerably improved by the admixture of Thio-indigo red. A very sharp reaction to ascertain the presence of even a trace of Thio-indigo red is obtained by treating the goods with a dilute solution of chromic acid, which completely destroys the indigo, leaving, after washing out, the whole quantity of Thio-indigo visible on the fibre.

#### THIO-INDIGO SCARLET R\* (Kalle).

This dyestuff belongs to the same group as Thio-indigo red B, and is represented by the formula—



It is obtained by condensing alpha-oxythionaphthene (see p. 662) with isatin,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \right\rangle \text{CO}$ . The chemical relation of the new colouring matter to Thio-indigo red is of a similar nature as that existing between indirubin and indigotin.

Thio-indigo scarlet R is furnished to the trade as a scarlet-red powder or paste practically insoluble in water and most other customary solvents. The solution in concentrated sulphuric acid is brown, and on diluting the dyestuff is separated in the form of a red precipitate. Thio-indigo scarlet R is soluble in chloroform, forming a solution giving the same brilliant fluorescence as Thio-indigo Red B; in fact, both products possess similar physical properties.

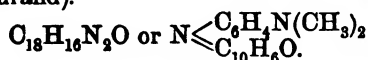
\* *Journ. Soc. Dyers and Col.*, 1907, p. 191.

*Application.*—Same as Thio-indigo red B. Although Thio-indigo scarlet R is not as readily reducible, it submits to reduction much more easily than indigo. The sodium sulphide bath is not recommended for the scarlet brand. It dyes a moderately bright scarlet, which also possesses excellent properties of fastness to light, washing, milling, alkalis, acids, and chlorine; the fastness to light and washing, however, is not quite as good as that of Thio-indigo red B.

**HELINDONE RED 3 B (M.L.B.). VAT RED B (B.A.S.F.). CIBA RED G\* (Ch. Ind. Basle).**

These dyestuffs are of similar constitution and properties as Thio-indigo red B, and are applied in the same manner. Vat red B dyes more bluish-red shades than Thio-indigo red B, and Helindone red 3 B still more bluish-reds, whereas Ciba red G is similar in shade to Thio-indigo scarlet R. The three brands work more readily on to the fibre than Thio-indigo red.

#### INDOPHENOL (Durand).

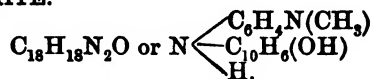


Indophenol, which has also been called *Naphthol blue* is an *alpha-naphthoquinonedimethylanilineimine*. It is obtained by the action of nitrosodimethylaniline on alpha-naphthol or by oxidising a mixture of para-aminodimethylaniline and alpha-naphthol.

Indophenol possesses basic properties and dissolves in acids; it is, however, a very unstable compound in acid solutions and no permanent salts can be prepared. It is immediately decomposed by concentrated sulphuric acid, more slowly by diluted acids, into naphthoquinone and dimethylparaphenylenediamine. Reducing agents, both acid and basic, readily convert the Indophenol into a leuco-compound, the Indophenol white (see below).

Indophenol is sold as a dark brown crystalline powder or as a dark blue paste with a bronze reflex. It is quite insoluble in pure or in alkaline water; but dissolves readily in alcohol, ether, or benzene, with a blue colour. Caustic alkalis have no action on the colour, diluted acids dissolve it with a yellow colour, the solution decomposes readily and yields on boiling the pungent smell of alpha-naphthoquinone. Concentrated sulphuric acid dissolves it with a brownish-yellow colour; on diluting with water a brown precipitate is obtained.

#### INDOPHENOL WHITE.



Indophenol white, or *dimethylparaaminophenylalphanaphthylamine*, possesses both basic and acid properties, and is readily converted into Indophenol by oxidising agents, such as bichromate, and even by atmospheric oxygen. It is prepared by reducing Indophenol with stannous acetate (10° Tw.), and is sold by the manufacturers of Indophenol as a yellowish-white paste for use in calico-printing in place of indigo. The commercial article is a compound with stannous oxide or stannous salt, which dissolves in boiling water and is not decomposed by acids; in alkaline solution it is readily converted into indophenol.

*Application of Indophenol and Indophenol White.*—Indophenol resembles indigo in being readily reduced in alkaline solutions to a leuco-compound, which is soluble in the alkaline liquor. The attempts made to dye with Indophenol alone by one of the vat-indigo methods were not very successful, because the fibre did not readily absorb the leuco-compound.

\* Ciba red G is produced by brominating Thio-indigo scarlet or a similar compound (G. Engi, *Chemiker Zeitung*, 1908, p. 1179).

But for some time Indophenol has been used in combination with indigo for the dyeing of cotton, wool, and union goods in the hydrosulphite vat. This colouring matter, however, has not found general application, as it does not offer sufficient advantages over indigo, and is too readily affected by acids.

Indophenol is nearly as fast to light and milling as indigo; fast to alkalies, but not to acids, and rubs less than indigo.

### THE INDANTHRENE-SERIES.

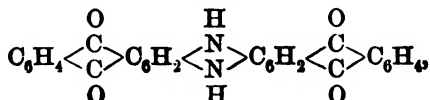
Indanthrene, Flavanthrene, Melanthrene, &c., are a series of vat colours, called after the first member Indanthrene, which was discovered by René Bohn, and brought into the market by the Badische Anilin- und Soda-Fabrik. The chemical constitution of a great number of Indanthrene products has been determined by R. Scholl.\* They are usually dyed in a strongly alkaline hydrosulphite bath and, therefore, serve exclusively for dyeing cotton (and other vegetable fibres), on which they yield colours of extraordinary fastness to light, washing, &c.

The series of *Algol colours* (Bayer) belongs chemically to the same group of vat colours.

In dyeing with the Indanthrene colours, contact with copper vessels or apparatus must be avoided. The chief essentials for satisfactory dyeing the Indanthrene colours are:—(1) Maintaining the correct temperature. (2) Sufficiently handling the goods in the bath to ensure even dyeing. (3) Avoidance of unnecessary oxidation through exposure to air during or immediately after dyeing. (4) The presence of sufficient alkali and hydrosulphite to keep the dyestuff in solution during the whole period of dyeing.†

#### INDANTHRENE (B.A.S.F.).

Indanthrene S is dihydroanthraquinone azine,



and is obtained by fusing  $\beta$ -aminoanthraquinone with caustic potash at 200° to 250° C. A leuco-compound is produced first, which, on boiling with water in the presence of air, is converted into anthraquinone azine, an insoluble blue crystalline body which formed the first product of the series, marketed under the name *Indanthrene X*, but now withdrawn from commerce. By reducing and purifying this product the brand *Indanthrene S* is produced, which, in vat dyeing—i.e., on reduction and re-oxidation—regenerates the anthraquinone azine (*Indanthrene X*).

*Indanthrene O* is prepared by the bromination of Indanthrene, and is a mixture of the di- and tri-bromo derivatives. It possesses the valuable property of resisting the action of hypochlorites of the ordinary strength.

*Indanthrene CD*, the dichloro derivative, also is fast to chlorine, but is only suitable for calico-printing.

Indanthrene S in the sublimated state forms beautiful coppery-blue crystals. The various brands are marketed as pastes insoluble in water, dilute acids and alkalies. The solution in concentrated sulphuric acid is yellowish-brown, and on diluting, the dyestuff is reprecipitated. By a reducing agent in alkaline solution, notably sodium hydrosulphite, Indanthrene is reduced and a blue solution is obtained which serves for dyeing the vegetable fibres; on exposure to air Indanthrene—i.e., anthraquinone azine—is regenerated and fixed in an

\* R. Scholl and H. Berblinger, *Berl. Ber.*, 1903, p. 3410, *et seq.*

† R. B. Brown, *Journ. Soc. Dyers and Col.*, 1906, p. 11.

extremely stable condition. The great fastness of the dye is explained by Scholl by the fact that both the reduction and the oxidation product are very much less stable and tend to revert to the form of Indanthrene.

*Application.*—Indanthrene is exclusively used for dyeing and printing cotton and other vegetable fibres, and is always fixed by re-oxidising on the fibre the previously reduced colouring matter. It is, therefore, a true vat-dye. The most suitable reducing agent for dyeing is sodium hydrosulphite, though in the East an alkaline mixture of ferrous sulphate and stannous chloride is also used for piece-dyeing. Indanthrene, on reduction, yields a blue vat, consequently the degree of reduction cannot be as easily judged as in the case of indigo; but this difficulty is easily overcome by practical experience. For printing, several methods are available; Indanthrene mixed with stannous oxide or other reducing agents and alkaline thickenings is printed on and steamed, or a paste containing Indanthrene, ferrous sulphate, stannous chloride, and tartaric acid is printed on, and the pieces, after drying, are passed in the open width through a bath of caustic soda (32° Tw.) at 70° to 80°, then through a cold soda bath, rinsed, soured, and soaped; the method used for indigo printing—*i.e.*, preparing with glucose and printing with Indanthrene and an alkaline thickening may also be employed.

*Dyeing Methods.*—The reducing agent, except in a special method of piece-dyeing to be described below, is always sodium hydrosulphite either in the form of the manufactured powder or prepared in solution from bisulphite and zinc powder. The bath is made alkaline with caustic soda and used at a temperature of 50° C. with Indanthrene C, or at 60° C. with Indanthrene S. If dyed much below the temperature given, solution is not complete, but if only slightly below, the only ill effect is imperfect exhaustion; if the temperature exceeds that stated, a partial decomposition and loss of dyestuff may occur. Indanthrene C if dyed above 50° C. loses in fastness to chlorine.

For 10 lbs. of cotton yarn about 150 litres (33 galls.) water and 3 litres ( $\frac{3}{4}$  gall.) caustic soda lye (52° Tw.) are required. After heating the bath so as to be 10° C. below the dyeing temperature, caustic soda, then the hydrosulphite, and finally, through a fine sieve, the dyestuff are added and brought into solution by gentle stirring. When viewed in a small glass-beaker or pipette the solution must be blue and clear; if it contains small coppery crystals these must be dissolved by adding more hydrosulphite. After heating the bath again to its initial temperature—*i.e.*, 50° C. for Indanthrene S and 40° C. for the "C" brand—the wet yarn is entered, turned ten minutes, and after raising the temperature by 10° C. (60° for "S," 50° for "C") it is turned again for a quarter of an hour. The yarn is then well wrung, rinsed immediately and without being exposed to the air, in water containing a slight quantity of hydrosulphite, and then thoroughly in pure water, soured off, well washed, and finally hot soaped. When less than 10 per cent. of dyestuff has been taken, there is little advantage in using the old dye-baths for further lots of yarn. For deeper shades the bath may be used for three or four successive lots, if freshened up with suitable quantities of colour, alkali, and hydrosulphite.

For the dyeing of compound shades, dyestuffs must be selected which can be applied at the same temperature.

If the colours come out streaky or uneven, they may be treated in an alkaline bath of hydrosulphite or, if this treatment should fail, a weak hypochlorite bath should be given and the colour then be restored with hydrosulphite.

**Loose cotton is dyed like yarn.**

For piece-goods a jigger is employed, in which the rollers are under the surface of the liquor. Caustic soda is first added to the bath and the piece given two ends at the required temperature; the hydrosulphite and the colour

mixed with liquor from the dye-bath are then added, and after stirring, dyeing proceeds for three-quarters to one hour. To produce very dark shades, after dyeing as above the liquor is run off into another vessel, and caustic soda lye (32° Tw.) is run into the jigger; 4 to 6 ends are given and the piece passed between squeezing rollers under light pressure. The soda is now run out and the old dye-bath brought again into the jigger. A suitable amount of Indanthrene and Flavanthrene (to deepen the shade) and the necessary quantity of hydrosulphite are added, and dyeing continued for three-quarters to one hour at 60° C. when the bath should be exhausted. Finally, the pieces are soured, soaped, &c. The object of the first dyeing is to ensure a certain degree of penetration, the further treatment fixes a maximum amount of colour on the surface; for a dark navy blue, about 30 per cent. Indanthrene S and 2½ per cent. Flavanthrene G are required, and this method of dyeing is specified for the "Blue Jean" used as sailors' collars in the German navy, on account of the excellent fastness to light, sea-water, rubbing, &c., of the resulting colour.

A special method of dyeing piece-goods without hydrosulphite is largely used in Japan. The goods are dyed on the dipping frame and reduction is brought about by means of ferrous sulphate and stannous chloride. A stock vat is prepared containing 5 kgs. (lbs.) Indanthrene, 10 litres (1 gall.) caustic soda (52° Tw.), 3 kgs. (lbs.) ferrous sulphate, and 600 grms. (10 ozs.) stannous chloride; the whole is made up to 25 litres (2½ galls.), and in half an hour is ready for use. The dye-bath contains altogether 6 litres (5 pints) caustic soda lye in 100 litres (10 galls.) water and a quantity of the stock vat, and is used at 70° to 80° C. for five to twenty minutes. The goods are then slightly rinsed, taken from the frame, soured to remove iron, and again well rinsed and soaped. Dark shades are dyed by dipping several times, rinsing the goods between each immersion.

Indanthrene S dyes a beautiful reddish-blue, Indanthrene C a very fine more greenish-blue, of excellent fastness to light, washing, alkalies, acids, perspiration, cross-dyeing, and all finishing operations. Even in pale shades the fastness to light is extremely good, the colour being scarcely affected by several months' exposure. The fastness to washing is equally good. When boiled with soap the colour becomes slightly redder, but repeated soaping brings about no further change. By boiling caustic soda in the kier under pressure there is a tendency for the colour to mark off and stain the white. This may be obviated by the addition to the caustic liquor of 2 to 3 grms. sodium bichromate per litre (¼ lb. per gallon). When the goods are boiled in the open kier, this precaution is not necessary. Indanthrene C and CD remain unaltered by weak hypochlorite solutions (chemicking), and the former finds an extended application in the dyeing of yarns for goods which are to be bleached in the piece. Indanthrene S is changed to green by the action of hypochlorites, but the colour is restored by a weak hydrosulphite solution. It becomes much faster to chlorine by passing through a weak caustic soda bath (¼ per cent. solution) and steaming two hours under 15 lbs. pressure; even steaming alone is beneficial. F. Erban\* recommends steaming for two hours at a pressure of 60 to 75 lbs. to make the colour perfectly fast to bleaching powder. When this treatment is adopted, the shade becomes less greenish, nearly the tone of indigo.

INDANTHRENE SC is a more recent brand which is dyed, like Indanthrene C, at 50° C. It dyes reddish-blue shades, slightly duller than Indanthrene S, over which it possesses the advantage of greater fastness to chlorine. It is to be used when the latter is not fast enough to chlorine and the "C" brand too greenish-blue in shade.

\* *Journ. Soc. Dyers and Col.*, 1906, p. 166.



threne, but not quite as fast to light, and becomes redder by chlorine, the original colour being restored by hydrosulphite.

**RUFANTHRENE B (B.A.S.F.)** is similar to Fuscanthrene B, but less reddish in shade, and not fast to chlorine.

**CYANANTHRENE B (B.A.S.F.).**

When beta-amino-anthraquinone is heated with glycerin in the presence of a dehydrating agent, the reaction does not stop at the formation of a pyridine ring (as in the case of Alizarin blue), a further molecule of glycerine taking part in the reaction, which gives rise to a new ring formation called the benzanthrene ring, and a new body is formed called benzanthrenequinoline,  $C_{20}H_{11}ON$ . By melting this body with caustic alkali Cyananthrene is produced.

Black paste, insoluble in water, alkalies and hydrochloric acid; solution in  $H_2SO_4$ , dark green; solution in hydrosulphite, blue-violet.

*Application and Properties.*—Same as Indanthrene. Cyananthrene, however, is best dyed at  $90^\circ C$ ., the bath being exhausted almost completely near the boiling temperature. When Cyananthrene is to be combined with Indanthrene and Melanthrene, it is best dyed near the boil, the liquor then being cooled, and after adding the other colouring matters, the dyeing being finished at  $60^\circ C$ . Cyananthrene resembles Indanthrene in fastness, and in addition it is fast to chlorine.

**VIOLANTHRENE B (B.A.S.F.).**

Violanthrene B is formed by melting with alkalies the product of the condensation of anthraquinone or anthranol with glycerine called benzanthrene,  $C_{17}H_{10}O$ . The new dyestuff is one of the few examples of a colour containing no nitrogen capable of dyeing cotton substantively.

Black paste, insoluble in water, alkalies, and hydrochloric acid; solution in  $H_2SO_4$ , blue-violet; solution in hydrosulphite, red-violet.

*Application and Properties.*—Same as Indanthrene. Violanthrene B is dyed most advantageously at  $60^\circ C$ . At  $90^\circ$  darker, but duller, shades are obtained. It dyes a dark violet, and is chiefly useful for Indanthrene, which it equals in fastness, being in addition fast to chlorine.

**VIOLANTHRENE C D and R EXTRA (B.A.S.F.).**

These are two more recent brands which equal Violanthrene B in general properties and also in fastness. Both are sold in the form of pastes. Violanthrene C D yields less dark violets, and the "R" brand much brighter and redder violets. Violanthrene C D is serviceable for calico-printing, and "R" extra may be dyed on the dipping frame in a vat with ferrous and stannous oxide.

**VIOLANTHRENE B S (B.A.S.F.).**

This dyestuff, also furnished in paste form, is distinguished from the "B" brand by its better solubility and greater concentration. It is, therefore, suitable for cop dyeing, and, like Indanthrene S, it may be dyed on the dipping frame. Its shade and fastness are equal to those of Violanthrene B.

**VRIDANTHRENE B or INDANTHRENE GREEN B (B.A.S.F.).**

This product is a nitro-compound of Violanthrene, and is supplied as a black paste insoluble in water, alkalies, or hydrochloric acid; the dry product dissolves in concentrated sulphuric acid with a dark violet colour. Hydrosulphite dissolves the dyestuff with a violet-blue colour.

*Application and Properties.*—Same as Indanthrene. Viridanthrene B is dyed to best advantage, like Indanthrene S, at  $60^\circ C$ ., and yields lush-green and dark green shades of about the same fastness; it is, however, not fast to chlorine, the colour being blackened by hypochlorites.

**OLIVANTHRENE (B.A.S.F.).**

Black powder, insoluble in water, alkalies, or hydrochloric acid; solution in  $H_2SO_4$ , brown; solution in hydrosulphite, brown.



*Application and Properties.*—Same as Indanthrene. Olivanthrene is dyed at 60° C., and yields olive shades of excellent fastness to all influences except chlorine.

**INDANTHRENE COPPER R** and **INDANTHRENE ORANGE R T** (B.A.S.F.).

These two colouring matters closely resemble each other, and are produced by condensation of acetylated amino- and diamino-anthraquinone with the aid of phosphorus oxychloride.

Brown paste, insoluble in water, alkalies, or hydrochloric acid; solution in  $H_2SO_4$ , brown; solution in hydrosulphite, yellowish-brown.

*Application and Properties.*—Same as Indanthrene. Indanthrene copper dyes reddish-brown (copper) shades. Indanthrene orange dyes brownish-oranges of excellent fastness to light, washing, alkalies, acids, and chlorine. Both are dyed best at 60° C., but may also be dyed like the following Anthraflavone.

**ANTHRAFLAVONE G** (B.A.S.F.).

Anthraflavone is produced by condensation of methylantraquinone.

Olive-yellow paste, insoluble in water, dilute acids, or alkalies; solution in  $H_2SO_4$ , red-violet; solution in hydrosulphite, brown.

*Application.*—The dye-bath is prepared for 100 lbs. of cotton yarn at 40° to 50° C. with 7½ litres (1 gall. 5 pints) caustic soda lye (52° Tw.), 9 to 22½ kgs. (20 to 50 lbs.) sodium sulphate (calcined), and 1·7 to 3·4 kgs. (3¾ to 7½ lbs.) hydrosulphite in powder. The dyestuff is added through a fine sieve, and when it is well dissolved, the yarn is entered and dyed one hour at 40° to 50° C., being turned from time to time. It is then rinsed, a little hydrosulphite being added to the first rinsing liquor, and acidulated, well rinsed again, and finally soaped at the boil. Anthraflavone dyed in this way yields a beautiful greenish-yellow shade of excellent fastness to washing and chlorine, but not fast to light.

**ALGOL COLOURS** (Bayer).

The colours of the Algol series, which have recently been brought into the market, are chemically related to the Indanthrene colours, and are applied in the same way to the vegetable fibres in the vat.

**ALGOL BLUE C F** and **3 G** (Bayer).

Black paste, insoluble in water, alkalies, and hydrochloric acid; solution in  $H_2SO_4$ , olive-brown; solution in hydrosulphite, blue.

*Application.*—Algol blue is dyed to best advantage in the hydrosulphite vat at 50° to 60° C., similarly to Indanthrene, or in a vat prepared with glucose and caustic soda. Algol blue C F dyes a fine blue, similar to Indanthrene C, of very good fastness to washing, alkalies, and acids, and also to light, but not so fast as Indanthrene; the shade by the action of chlorine becomes greenish, and is not entirely restored by hydrosulphite. Algol blue 3 G dyes a more greenish-blue, which is also very fast to washing, alkalies, and acids, but the shade is deteriorated by severe alkaline washing; the fastness to light is approximately the same as that of the "O F" brand; Algol blue 3 G is not fast to chlorine. For calico-printing Algol blue may be applied in the same way as Indanthrene.

**ALGOL GREEN B** (Bayer).

Black paste, insoluble in water, alkalies, and hydrochloric acid; solution in  $H_2SO_4$ , green; solution in hydrosulphite, dull blue.

*Application.*—Same as Algol blue. Algol green dyes a bluish-green shade of the same fastness as Algol blue; by chlorine the colour is destroyed.

**ALGOL RED B** (Bayer).

Brown paste or powder, insoluble in water, alkalies, or hydrochloric acid; solution in  $H_2SO_4$ , violet; solution in hydrosulphite, orange-red.



but are less liable to change in strong mineral acid solutions; hence they are prepared with an excess of acid, and the solutions are kept acid. The successful preparation of azo-compounds of all kinds mainly depends on the purity of the diazo-compounds.

The diazo-compounds do not combine with the phenols in the presence of strong mineral acids. In manufacturing azo-colours on the large scale (away from the fibres) the diazo-solution is run in a thin stream into the alkaline solution of the phenol. The mineral acid of the former is saturated by the alkali of the latter, and the formation of the azo-colour takes place before the diazo-compound has decomposed. In dyeing, this process is not applicable, since it is impossible to charge the phenol in the fibre with enough alkali to neutralise the acid. The Hoechst Farbwerke have introduced an important modification of this process, which was first worked out by G. Galland. It is based on the fact that acetic acid does not strongly retard the process of combination; in this method sufficient sodium acetate is added to the diazo-compound to convert the free mineral acid into the sodium salt, and to liberate the acetic acid, which becomes more or less saturated by the excess of alkali used with the phenol.

*Application.*—The insoluble azo-colours are almost exclusively produced on the cotton fibre. Linen and the other fibres can also be dyed with them, but these colours have not been practically applied to them nor to wool and silk. They are largely used in calico-printing.

Paranitraniline (red) only is used extensively for yarn and piece dyeing, while alpha-naphthylamine (claret) and dianisidine (blue), more recently also *p* chloroanisidine (scarlet), are used to a minor extent for piece dyeing; the other diazo-compounds are not very suitable for dyeing, being either not stable enough, or coupling too slowly or producing loose colours; some, however, are extensively used in calico-printing. The insoluble azo-colours are not produced on loose cotton and rarely in machine dyeing for the reason that level colours are very difficult to obtain.

The first to produce insoluble azo-dyes on the fibre was Robert Holliday, who in 1880 introduced a class of colours dyed on cotton yarn and known as the "vacancine" colours. For some years these colours were dyed on cotton warps by Messrs. R. Holliday & Co., of Huddersfield, and Messrs. W. Grandage & Co., of Bradford.

Beta-naphthol is the only phenol which finds practical application in dyeing or printing, the other phenols being not suitable, alpha-naphthol, *e.g.*, yielding colours sensitive to alkalies. 2:7 naphthol monosulphonic F is sometimes used in combination with beta-naphthol for shading.

The insoluble azo-colours (especially those obtained from beta-naphthol) are very fast to washing and alkalies; they do not bleed at all, but are liable to rub, especially if not properly dyed.

They are also fast to acids with the exception of Dianisidine blue which is very sensitive to them. The fastness to light is not great, as a rule, except Paranitraniline red, Naphthylamine claret, *p* Chloroanisidine scarlet which are very satisfactory; it can be improved by treatment with a boiling solution of copper sulphate, but usually the shade is greatly altered by such treatment (see below). Some of the colours are volatile, and slowly volatilise from the fibre; but those which are obtained from beta-naphthol are free, or almost free, from this defect, and are, moreover, quite insoluble in caustic alkalies; whereas the compounds from alpha-naphthol and other phenols are soluble. The beta-naphthol colours are chiefly used both for their superior fastness and for the brightness of their shades.

Mercerised cotton, as with many other colouring matters, is dyed a much deeper shade than ordinary cotton, thus allowing a considerable economy of

naphthol and base (diazo-compound). According to A. G. Green,\* mercerised cotton, unlike ordinary cotton, has a decided affinity for beta-naphthol which it can take up from solutions (like a dyestuff), finally leaving the bath nearly exhausted.

The production of the insoluble azo-colours in the fibres is effected in two stages—(1) Impregnation of the fibre with the phenol; (2) Developing of the colour.

It is essential that the proper quantities of the various substances be used, as otherwise no useful colour or no colour at all is obtained; the dyeing of these colours requires the greatest exactness.

The following is the process applicable for all bases and phenols, aniline being chosen as an example for the reason that it is the simplest of all bases coming into consideration and beta-naphthol for being the most important phenol. Later on the production of the most important colours is fully discussed.

(1) *Impregnating*.—Beta-naphthol, as mentioned before, is used almost exclusively and in addition 2:7 naphthol sulphonic acid F. But the other phenols may be applied in the same way.

*Stock Solution for Cotton Yarn*.—1,440 grms. of beta-naphthol (previously broken up into small lumps) are dissolved in sufficient caustic soda (400 grms. of pure caustic soda or correspondingly more of the weaker commercial articles) and 2 to 5 litres of hot water. An excess of alkali is not injurious. When the naphthol has dissolved, the liquor is diluted to 10 litres. This diluted liquor may be called "stock liquor." One litre of stock liquor is diluted with 5 to 10 litres of water and 400 grms. of soda ash are added. For brightening the colours stannate of soda, Turkey-red oil, and other alkaline or neutral substances may be added to this solution. The addition of oil to the naphthol bath was patented by R. Holliday (Brit. patent, 1889, No. 20,064).

*Cotton hanks* are impregnated with the naphthol solution in lots of 2 lbs. each, and after each lot 50 c.c. of stock liquor and 20 grms. of soda ash are added to the bath to restore the strength.

It is essential that the material be impregnated very evenly; hence it is well to treat hanks in a tramping machine (see p. 584) which does both the steeping and the wringing. The depth of the ultimate colour depends chiefly on the quantity of naphthol which has been taken up by the fibre in this operation. Hence, stronger or weaker solutions may be used; but the strength must be preserved uniform to obtain equal shades.

*Cotton piece goods* are treated in the padding machine. The liquor may be prepared as before, but less diluted. Since, however, in this case a strong causticity of the liquor is less objectionable to the workmen, it may be prepared by dissolving 1,440 grms. of naphthol in 5 litres of hot water containing 800 grms. of caustic soda (100 per cent. NaOH), and diluting to 100 litres. The fabric is padded with this solution.

The impregnated material (yarn or piece goods) is immediately well dried, otherwise the naphthol solution would be washed out in the developing bath and a poor irregular colour result. It must be dried quickly, otherwise it becomes brownish, and the colours are not satisfactory. The material should be worked up soon, and should, until the developing, be carefully handled with dry hands and protected against water drops and acid vapours.

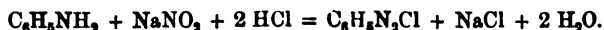
Lauber and Caberti recommend, in order to prevent the material from becoming brownish, to add to the naphthol solution a solution of antimony oxide in caustic soda lye to which some glycerin has been added. The naphthol bottom thereby is preserved for a considerable time. Tartar emetic or another antimony salt, together with an equal weight of glycerin, is dissolved in water, and caustic soda lye is added until the precipitate formed is re-dissolved

\* *Journ. Soc. Dyers and Col.*, 1898, p. 95.

About 25 per cent. antimony salt of the quantity of naphthol should be added. Naphthol L C (Bayer) is such a preparation with antimony. The addition of antimony is, however, rarely used owing to the expense, the prepared cotton being worked up as rapidly as possible. M. v. Gallois has proposed the use of glucose for the same purpose which acts nearly as well, but is also rarely employed.

(2) *Diazotising*.—The preparation of the diazo-solution requires great exactness.

One equivalent of the base requires one equivalent of sodium nitrite and two equivalents of acid for complete diazotisation, according to the equation:—



Since, however, the diazotisation proceeds better, and the diazo-compound is more stable in the presence of an excess of acid, about three equivalents of acid are used.

The equivalents of the principal bases in use are given below:—

Aniline, 93.	Anisidine, 123.	Aminoazobenzene, 197.
Nitraniline, 138.	Chloroanisidine, 157.5.	Aminoazotoluene, 225.
Toluidine, 107.	Phenetidine, 137.	Benzidine, 92.*
Nitrotoluidine, 152.	Nitrophenetidine, 180.	Tolidine, 106.*
Xylidine, 121.	Naphthylamine, 143.	Dianisidine, 122.*
Cumidine, 135.		

The equivalent of hydrochloric acid gas (HCl) is 36.5. The commercial products, however, contain but 28 per cent. (for 28° Tw.) or 32 per cent. (for 32 Tw.) of HCl; the equivalent of hydrochloric acid, 28° Tw., is 130, and that of acid, 32° Tw., is 114. The hydrochloric acid referred to below will be that which has the strength 28° Tw., the equivalent of which is 130. The equivalent of sodium nitrite is 69; but as the commercial article contains impurities, and as a small excess of the nitrite is required, the equivalent 75 is more suitable; 150 grms. of sodium nitrite are dissolved in water, and the solution is diluted to 1 litre, so that it has double the standard strength. In the following data it is this solution of 150 grms. of nitrite per litre that is referred to.

*Diazotisation of Aniline*. †—93 grms. of aniline are mixed with 390 grms. of hydrochloric acid (28° Tw.) and 200 c.c. of water; the solution is cooled by adding ice directly to the liquor; 500 c.c. of the nitrite solution are added gradually while stirring continuously; the temperature must not rise beyond 5°.

When all the nitrite has been added, iodide-starch ‡ paper must be turned blue *instantaneously* by a drop of the solution through liberation of iodine; should it not change, either more nitrite or more acid must be added. To ensure accuracy, *this test should be made every time*. A small excess of nitrite is not injurious; but any copious evolution of nitrous fumes is not only an indication of careless working, but will tend to dull the colour through the formation of nitrosanaphthol and to diminish the stability of the diazo-solution § (see below).

\* Benzidine, toolidine, and dianisidine are diamines, since they contain the amido-group  $\text{NH}_2$  twice in their molecule; hence their equivalents are only one-half of the molecular weights, the latter being 184, 212, and 244 respectively. The metrical system of weights and measures will be used in the sequel. They can readily be converted into the English system when required.

† This is merely given as a simple example. The colour obtained with aniline though an intense orange is never used practically on account of its volatility.

‡ The iodide-starch paper is prepared by dissolving a few grammes of iodide of potassium in 1 litre of thin starch paste, saturating filter paper in this solution, and drying in pure air. It is advisable to keep this paper in a well-closed glass bottle. Iodide-starch paper which has been kept too long may show the iodine reaction on moistening even in the absence of free iodine and should not be used.

§ Great care should be taken not to inhale these red vapours since they act as an exceedingly dangerous poison.

The diazo-solution is filtered or strained through calico after a few minutes' standing and the filtrate is diluted to 10 litres. A short time before using the diazo-solution add 300 grms. of sodium acetate in order to neutralise the mineral acid. No more diazo-solution should be mixed with the sodium acetate than will be worked up in the next half hour, and it should be kept below + 5° C.; otherwise it will rapidly decompose and produce irregular colours.

The other bases named in the foregoing list are diazotised exactly in the same way, except that instead of 93 grms., the number of grammes expressed by their equivalents are used; for example, 107 grms. of toluidine or 143 grms. of alpha- or beta-naphthylamine or 92 grms. of benzidine. The naphthylamines, however, must be brought into a suitable form, before they can be diazotised. (About *p* nitraniline, see below).

Melt 143 grms. of *alpha-naphthylamine* in 2 litres of hot water, add 200 grms. of hydrochloric acid (28° Tw.) and heat the mixture on the water-bath, until all is dissolved; then add 190 grms. of hydrochloric acid and stir until quite cold. A paste of the hydrochloride is thus obtained, but all goes into solution again after the nitrite has been added. Into the well-cooled liquor pour 550 c.c. of the nitrite solution, introducing it below the surface, and stir well; the temperature should not rise above + 3° C. After fifteen minutes' standing, filter, and dilute the filtrate to 10 litres; add 300 grms. of sodium acetate a short time before using.

The sulphate of alpha-naphthylamine is very convenient for use as it can be prepared in the shape of a dry powder. It is marketed as Alpha-naphthylamine salt S (M.L.B.), of which 192 grms. require for diazotising 100 grms. conc. sulphuric acid and 520 c.c. nitrite solution.

Impure alpha-naphthylamine, according to E. Kopp,\* is liable to produce black spots, especially under the influence of sunlight. It is, therefore, recommended to use the purest qualities and to avoid the access of direct sunlight during the treatment of the material with the diazo-compound and before washing.

Dissolve 143 grms. of *beta-naphthylamine* on the water-bath in 130 grms. of hydrochloric acid (28° Tw.) and 2 litres of water, filter the hot solution and stir rapidly until quite cold. To the resulting greyish-white paste add 260 grms. of hydrochloric acid and sufficient ice; and then 550 c.c. of the nitrite solution; the temperature should not rise beyond + 3°. After fifteen minutes' standing, filter, make up to 10 litres, and add 300 grms. of sodium acetate before using.

Some bases, the hydrochlorides of which are sparingly soluble in water, —*e.g.*, the nitranilines and nitrotoluidines may be mixed with advantage with the required amount of nitrite and then added to the solution of acid. The Farbwerke Hoechst have prepared mixtures of these bases with the required amount of nitrite, which are designated with the letter N (= nitrite); for instance, aminoazobenzene N. These mixtures are readily diazotised on being added to water containing the necessary quantity of acid. Instructions for use are given for these preparations; the required quantities of acid, &c., can also be calculated from the above data.

Aminoazobenzene, aminoazotoluene, and *p* nitro *p* phenetidine (blue-red O —M.L.B.) are also best diazotised by being first intimately mixed with the nitrite and added to the acid solution which should be kept at about 15° C.

In order to save the dyer the labour of diazotising, numerous attempts have been made to prepare stable diazo-compounds, and these have been especially successful with *p* nitraniline, the diazo-compound of which by itself is distinguished by great stability. Various additions, which do not influence the

\* *Journ. Soc. Dyers and Col.*, 1895, p. 151.

final shade, such as kieselguhr (diatomaceous earth), sodium sulphate, zinc chloride, oxalic acid, nitrobenzene sulphonic acid, naphthalene sulphonic acids, &c., may be made for this purpose. The only important products of this kind are the Azophore preparations, especially Azophore red P N (M.L.B.), and Nitrazol C (Cassella). *Azophore red P N* is diazotised *p* nitraniline with an admixture of aluminium sulphate and sodium sulphate. *Nitrazol C* is *p* nitraniline diazotised in a solution of strong sulphuric acid and mixed with sufficient sodium sulphate so as to produce a stable solid mass.

A different product is *Nitrosamine red* (B.A.S.F.) which represents *p* nitrophenyl nitrosamine sodium,  $\text{NO}_2\text{C}_6\text{H}_4 \cdot \text{N}=\text{N} \cdot \text{ONa}$  (?), produced by the action of caustic soda on *p* nitrodiazobenzene chloride. As such it does not react with the alkaline solution of beta-naphthol, but is readily reconverted into the diazo-compound by the action of acid and may be used in acid solution like the ordinary diazo-compound. It also passes over into the diazo-compound by the action of the atmospheric carbonic acid, and Caberti and Peco have, therefore, proposed to treat the fibre in succession with beta-naphthol and the nitrosamine, but the process does not give much satisfaction.

(3) *Developing*.—The impregnated material is turned a few times in the diazo-solution, prepared as stated above, or in case of pieces run through and allowed to remain with the diazo-solution in it before washing off. It is important that at this stage the pieces should be protected from the action of direct sunlight, and then thoroughly washed in water. To prevent rubbing, it must be soaped at 60°, and washed again in water. The diazo-solution may be used continuously; it should be thrown out, however, if it begins to decompose rapidly. A good colour is obtained by using the exact proportions of base, acid, nitrite, acetate, naphthol, and alkali, and working carefully. The production of these colours requires, however, unusual exactness, and cannot be effected by an ordinary workman without the help of an educated dyer.

Beta-naphthol produces with the most frequently employed bases (in the form of diazo-compounds) the following shades:—

Name of the Base.	Colour with $\beta$ -naphthol.	Name of the Base.	Colour with $\beta$ -naphthol.
Aniline.	Orange-yellow.	$\alpha$ -Naphthylamine.	Bluish-claret.
<i>p</i> Toluidine.	Yellow-orange.	$\beta$ -Naphthylamine.	Turkey-red.
<i>m</i> Nitraniline.	Fiery yellow-orange.	Aminoazobenzene.	Red.
<i>p</i> Nitraniline.	Scarlet.	Aminoazotoluene.	Yellowish-claret.
Nitro- <i>p</i> -toluidine.	Red-orange.	Benzidine.	Brown (puce).
<i>p</i> Chloroanisidine.	Scarlet.	Tolidine.	Brown (puce).
<i>o</i> Nitro- <i>p</i> -phenetidine.	Bluish-red.	Dianisidine.	Violet.

With alpha-naphthol brownish-orange to dark brown shades are obtained.

The colours can be improved in fastness to light by treatment with a boiling solution of copper sulphate, or with ammonio-cupric solutions at 40° to 50°. The shades are thereby more or less altered (see pp. 384 and 683).

#### PARANITRANILINE RED, PARA RED, or ICE RED.

An excellent bright and fast red is obtained with diazotised *p* nitraniline and beta-naphthol. The colour will be brighter and bluer the less *o* or *m* nitraniline there is in the base, which is determined by the melting point; pure *p* nitraniline melts at 147° C. The beta-naphthol should also be very pure and free from alpha-naphthol. A more bluish-red is obtained by replacing a part of the beta-naphthol by (2 : 7) naphthol sulphonic acid F (up to 8 per cent.). The alteration of shade effected by this addition is explained by Schwalbe and Hiemenz by physical changes, the azo-compound of the sulphonic acid being removed by the hot soaping following the developing.\*

\* *Zeitschrift für Farbenindustrie*, 1906, p.134.

For this red, which is of great practical importance for the dyeing of both yarn and piece-goods, very exact formulæ have been given by various colour works, of which the following may be briefly recapitulated :—

(1) *Paranitraniline Red on Yarn*.—For 100 lbs. of yarn (L. Cassella & Co.) : The yarns are first boiled with caustic soda or soda ash, then washed and dried. 1,000 grms. beta-naphthol (or for a more bluish-red, 1,000 grms. naphthol R C (Cassella) or a mixture of about 900 grms. beta-naphthol and 100 grms. (2 : 7) naphthol sulphonic acid F) are mixed with 1,000 grms. caustic soda (75° Tw.) and dissolved by the addition of 10 litres boiling water. In another vessel 2,500 grms. castor-oil soap\* are dissolved in 10 litres boiling water. An equal quantity of Turkey-red oil may be used in place of the castor-oil soap ; with the latter, however, bluer and brighter shades are obtained.

The solutions of naphthol and soap are mixed and diluted to 60 litres. This solution is used at a temperature of about 40° to 45° C. For working by hand a trough, as shown in Fig. 66, may be used with advantage. The trough is placed under a wringing post and the liquor filled into the bowl. At first, 15 litres of the naphthol-soap liquor are put into the bowl and 2 lbs. of yarn are passed through ; then 900 c.c. of liquor are added and another 2 lbs. of yarn passed through, and so on, until the whole lot of 100 lbs. has been passed. Then the yarn, in lots of 2 lbs. at a time, is passed once more through the liquor, wrung off, wrapped up in calico, and very thoroughly hydro-extracted.

The yarn is then hung up rather loosely over square sticks (not more than 1 lb. for each stick), dried sharply, and then developed without delay. When the yarn is dried on fresh sticks not yet saturated with naphthol, it may show yellow rail marks ; in order to avoid this fault, 3 litres of an aqueous solution of dextrine 1 : 2 should be added to the naphthol solution and 600 c.c. of the dextrine solution put into the bowl of the trough before beginning with a fresh lot of 100 lbs. of yarn. Separate drying rooms free from any acid vapours are recommended for drying the impregnated yarn.

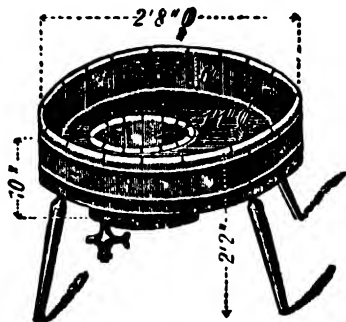


Fig. 66.

For developing with diazotised *p* nitraniline, hydrochloric acid and caustic lye of the right strength must be used, free mineral acid preventing the coupling, whilst free caustic soda will decompose the diazo-compound. A large excess of nitrite should be avoided, the stability of the diazo-solution being considerably diminished by free nitrous acid.† The hydrochloric acid should be free from copper and iron, these metals having a dulling effect on the red.

850 grms. pure *p* nitraniline are mixed with 3 litres boiling condensed water and dissolved with 2 litres hydrochloric acid (32° Tw.). This solution is run in a thin stream with constant stirring into 20 litres very cold water. When the solution has cooled off to at least 14° C., 500 grms. sodium nitrite dissolved in 2 litres cold water are added in one lot while stirring, and the clear solution resulting after ten minutes is diluted to 42 litres. In another vessel either 570 c.c. caustic soda lye (75° Tw.), or for a more bluish-red

\* To prepare castor oil soap, boil 10 kgs. castor-oil (best quality) with 8½ kgs. caustic soda lye (36° Tw.) for one hour, allow to cool for five hours, add 2½ kgs. hydrochloric acid (32° Tw.), boil again half an hour, and, after it has become cool, draw off the salt solution.

† C. G. Schwalbe, *Journ. Soc. Dyers and Col.*, 1905, p. 345.



500 c.c. of this lye and 1 kg. sodium acetate, or for a still bluer red 2 kgs. sodium acetate without lye are dissolved in 18 litres cold water for neutralising the mineral acid of diazo-solution. The diazo-solution keeps best when neutralised with caustic soda in the right quantities, but the red is then more yellowish than when sodium acetate is used.

For developing, a trough similar to that recommended for mordanting, but with a slightly larger bowl (16 inches in diameter and 10 inches deep and with a holding capacity of  $6\frac{1}{2}$  galls.), may be used. The bowl is charged with 12 litres very cold water, 10 litres of the diazo-solution, and  $4\frac{1}{2}$  litres of the neutralising liquor. Two lbs. of the impregnated and dried yarn are passed through, wrung off, passed through again (altogether about one minute), and wrung off finally. Then 630 c.c. of the first and 270 c.c. of the second liquor are added and again 2 lbs. of yarn passed through, and so on until the whole lot of 100 lbs. has been passed.

The yarn is then thoroughly rinsed and soaped at the boil. The red turns considerably bluer by the hot soaping which may be repeated to advantage, the yarn then being rinsed hot between the two soapings.

No ice is needed when very cold water is used. If, however, the temperature of the dye-house should be above  $20^{\circ}$  C., it is well to cool the diazo-solution by adding small pieces of ice.

Instead of diazotising *p* nitraniline, Nitrazol C (Cassella) may be used in the same way, the diazo-solution being prepared by dissolving  $5\frac{1}{2}$  kgs. Nitrazol C in 30 litres cold water, passing through a fine hair sieve and diluting as above to 42 litres. The neutralising liquor is prepared by dissolving 1,900 c.c. caustic soda lye ( $75^{\circ}$  Tw.) alone, or 1,700 c.c. of this lye, together with 1,200 grms. sodium acetate in 18 litres cold water.

The Hoechst Farbwerke (M.L.B.) recommend for a more yellowish-red 20 to 25 grms. beta-naphthol, 28 to 35 grms. caustic soda lye ( $36^{\circ}$  Tw.), and 60 to 75 grms. Turkey-red oil 50 per cent. (sodium salt); for a more bluish-red 20 to 25 grms. Naphthol R, 40 to 50 grms. caustic soda lye ( $36^{\circ}$  Tw.), and 60 to 75 grms. Turkey-red oil for 1 litre of liquor. An increased quantity of oil acts favourably. With Azophor the sulphonated oil is preferable to castor-oil soap (p. 679). For developing, 4,480 to 5,600 grms. Azophor red PN (M.L.B.) are dissolved in 30 litres cold water, stirring fifteen to thirty minutes, allowing to stand one to two hours and filtering the clear solution through cotton cloth; the sediment is washed with 10 litres water, so as to yield 40 litres clear liquor, which before use is neutralised with 2 to  $2\frac{1}{2}$  litres caustic soda lye ( $36^{\circ}$  Tw.), diluted with  $7\frac{1}{2}$  to 8 litres water. For developing, 25 litres of the neutralised diazo-solution and 25 litres water are put into the trough, and 2 lbs. yarn are passed through; the bath is freshened up with  $\frac{3}{4}$  litre of the diazo-solution and again 2 lbs. yarn are passed through, and so on. After developing, the colour is given some time to form completely, and then the yarn is rinsed and soaped, for yellowish-red, with 1 to 2 grms. soap; for bluish-red, with 2 grms. soap and  $\frac{1}{4}$  gm. soda-ash per litre, ten to fifteen minutes at  $60^{\circ}$  C.

The following instructions are given for Paranitraniline S (Bayer)—i.e., *p* nitraniline sulphate, containing 50 per cent. base:—For 100 lbs. of yarn 1 kg. beta-naphthol are dissolved in 1 kg. caustic soda lye ( $67^{\circ}$  to  $76^{\circ}$  Tw.), and 20 litres boiling water, adding 3.5 litres perfectly soluble Turkey-red oil 50 per cent., and 0.7 kg. sodium aluminate dissolved in 7 litres water; the whole is diluted to 55 to 65 litres. For a more bluish-red, 1 kg. Naphthol A R (Bayer) is used instead of beta-naphthol. The trough is filled with 14 litres of the solution, and after passing 2 lbs. of yarn each time, 900 c.c. solution are added again. 1.5 kgs. Paranitraniline S are mixed with 1 litre hydrochloric acid ( $32^{\circ}$  to  $34^{\circ}$  Tw.), adding 3 litres boiling water, and short boiling. This

solution is stirred in a thin stream into 40 litres cold water, and diazotised by adding in one lot 410 grms. sodium nitrite dissolved in 4 litres cold water; the diazo solution, immediately before use, is neutralised with 400 grms. soda ash and 750 grms. sodium acetate in 8 litres water, and diluted to 56 to 65 litres. The diazo-solution is used in the same quantities as the naphthol solution.

For Nitrosamine red (B.A.S.F.) the following instructions are given:— For 50 lbs. yarn, 650 grms. beta-naphthol, 650 grms. caustic soda lye ( $72^{\circ}$  to  $77^{\circ}$  Tw.), and 2 kgs. Turkey-red oil F are dissolved and diluted to 23 litres. For the first lot of 2 lbs. yarn,  $7\frac{1}{2}$  litres of this solution and  $7\frac{1}{2}$  litres water are used, and for every fresh lot of 2 lbs. 600 c.c. naphthol solution are added afresh. For developing, 2,400 grms. Nitrosamine in paste are mixed with 15 litres water ( $18^{\circ}$  C.) and 900 grms. hydrochloric acid ( $32^{\circ}$  Tw.). A pale yellow precipitate is formed, which should dissolve within ten minutes, leaving only a slight quantity of buff-coloured froth, which is scummed off. Immediately before use 800 grms. sodium acetate in 10 litres water are added, and the whole is diluted to 32 litres. The temperature of the liquor should be kept

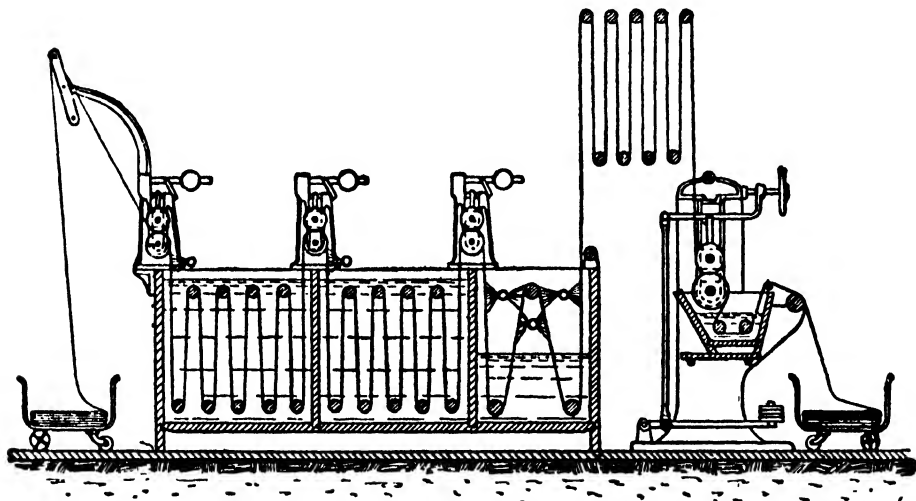


Fig. 67.

between  $15^{\circ}$  and  $22^{\circ}$  C. For developing the first 2 lbs. yarn, 7 litres of this solution and 8 litres water are required, and for each further lot 1 litre of solution is added. After developing, the yarn is soaped for fifteen minutes at  $60^{\circ}$  C. in a solution of 1,200 grms. neutral soap in 350 litres water; for bluer shades of red, with soft soap, or it is soaped a second time with 5 kgs. Turkey-red oil F and 600 grms. soda ash.

2. *Paranitraniline Red on Piece Goods.*—This is dyed practically like yarn. For a bluish-red, for instance,  $2\frac{1}{2}$  kgs. beta-naphthol and 200 grms. (2:7) naphthol sulphonic acid F are mixed with  $2\frac{1}{2}$  kgs. caustic soda lye ( $75^{\circ}$  Tw.), and dissolved by adding  $3\frac{3}{4}$  litres boiling water;  $2\frac{1}{2}$  litres cold water and 5 kgs. castor-oil soap (see p. 679), dissolved in 25 litres hot water, are added, and the whole is diluted to 100 litres. A more yellowish-red is obtained by omitting the addition of the naphthol sulphonic acid without otherwise altering this recipe. The impregnating is best done in a padding machine with three squeezing rollers. The trough is filled with the naphthol solution, which is replenished in proportion to the quantity absorbed by the pieces. The pieces should be

developed as soon as possible after the preparing and drying. The developing is carried out in a padding machine, a suitable form of which is shown in Fig. 67. 1,400 grms. *p* nitraniline are mixed with 10 litres boiling water, and perfectly dissolved by adding 2 litres 800 c.c. hydrochloric acid (36° Tw.). This solution is stirred into 25 litres cold water, cooled off to 10° to 14° C. by adding about 5 kgs. ice, and diazotised by adding in one lot 7 litres 800 c.c. of a 10 per cent. solution of sodium nitrite. The clear solution resulting after a few minutes is diluted with cold water to 75 litres. For neutralising, a solution of 3 kgs. sodium acetate in 25 litres is prepared, using 3 parts of diazo-solution and 1 part of acetate solution. The trough of the padding machine is filled with the developing liquor, the temperature of which should not exceed 14° C., and while the pieces are passing through, fresh solution corresponding to the quantities used up (3 parts diazo-solution and 1 part acetate solution) is added. After passing through the liquor the pieces are well squeezed, and run through the air for several yards over guiding rollers to give the dye time to develop completely. They are then well washed in several washing boxes, soaped at the boil, well rinsed, and dried.

**ALPHA-NAPHTHYLAMINE CLARET.**—Owing to the rapid decomposition of the diazotised alpha-naphthylamine, this colour cannot be produced evenly on yarn, and is exclusively dyed on cotton tissues; in this case also quick working is advisable. According to the Hoechst Farbwerke, for light shades 70 grms. beta-naphthol and 250 c.c. caustic soda lye (36° Tw.) are used; for dark shades 250 grms. beta-naphthol and 500 grms. lye; and for a more brownish-red (puce), 220 grms. beta-naphthol, 30 grms. alpha-naphthol, 400 c.c. lye, and 500 grms. tragacanth thickening are employed each time, together with 750 grms. tragacanth thickening (60 : 1,000) in 10 litres. For dark colours 192 grms. Alpha-naphthylamine salt S powder (M.L.B.) are diazotised (see p. 677), in presence of 1,000 grms. tragacanth thickening and 300 grms. sodium acetate diluted to 10 litres. The working is like that described for *p* nitraniline red. British gum (25 grms. to 1 litre) may be used in place of gum tragacanth.

Alpha-naphthylamine furnishes with beta-naphthol a bluish-red or claret, fairly bright, and fairly fast to light, and very fast to washing, acids, and alkalis. The colour is of special importance to the calico-printer for discharging with sulphoxylate formaldehyde.

**BETA-NAPHTHYLAMINE**, diazotised, produces with beta-naphthol a bright, but not very fast, Turkey-red shade.

**CHLOROANISIDINE P (B.A.S.F.)**—*i.e.*, the hydrochloride of *p* chloroanisidine (Cl : 1, NH<sub>2</sub> : 3, O. CH<sub>3</sub> : 4)—diazotised and coupled with beta-naphthol on cotton, produces very bright scarlets of good fastness to light, washing, and chlorine. Its fastness is nearly the same as that of *p* nitraniline red, but it is less readily discharged by hydrosulphites. For preparing the diazo-solution, 19.5 grms. Chloroanisidine P are dissolved in 500 c.c. water and 15 grms. hydrochloric acid 30 per cent. After cooling to 5° to 10° C., a solution of 7 grms. sodium nitrite in 100 c.c. water is added, and the mixture is stirred for ten to fifteen minutes until the diazotisation is complete. This solution keeps very well. Immediately before use 20 grms. sodium acetate dissolved in water are added, and the whole is diluted to 1 litre. The diazo-solution must not be filtered before use. When the base of Chloroanisidine P is used, the quantity of hydrochloric acid is increased to 30 grms. The naphthol solution is prepared by dissolving 15 grms. beta-naphthol and 15 grms. caustic soda lye (75° Tw.) in 200 c.c. hot water, adding 50 c.c. Turkey-red oil F, and diluting to 1 litre. The working is the same as described for Paranitraniline red.

**DIANISIDINE (NAPHTHOL) BLUE.**—Diazotised dianisidine with beta-naphthol furnishes a dull violet, which, according to Fr. Stork, by a treatment with copper compounds is converted into a very fine and fast blue, only

sensitive to strong alkali and weak acids, and also to the action of perspiration. By the addition of beta-oxynaphthoic acid (melting point 216° C.), beta-naphthol sulphonic acid F or Sch. or dioxynaphthalene 2 : 3, 2 : 6, or 2 : 7, darker and redder blues are obtained, which are less sensitive to acids and perspiration. Naphthol D (M.L.B.) contains an addition of one of these substances. Dianisidine diazotised is marketed in a stable form as Azophor blue D (M.L.B.). Dianisidine blue, like Naphthylamine claret, cannot be produced well on yarns, and is too sensitive to acids to be frequently used on piece goods, but finds some employment in calico-printing.

**PARANITRANILINE BROWN.**—This colour, although not used in dyeing proper, may be briefly described according to the instructions published by the Hoechst Farbwerke:—250 grms. beta-naphthol, 500 c.c. caustic soda lye (36° Tw.), 300 grms. Para soap P N (M.L.B.)—*i.e.*, castor-oil soap—and 1,000 grms. alkaline copper solution are dissolved in water and diluted to 10 litres. The alkaline copper solution is prepared with 1,000 grms. cupric chloride solution (76° Tw.), 500 grms. tartaric acid, 1,200 c.c. caustic soda lye (75° Tw.), and 400 c.c. glycerin. The cotton is prepared with the naphthol solution, dried, and developed with diazotised *p* nitraniline. The ready-dyed Paranitraniline red may also be converted into brown by boiling in a solution of copper sulphate; but this method is less advantageous. It is not recommended to add the copper sulphate to the diazo-solution, which thereby loses in stability. The colour is very fast to light and washing, but not to perspiration.

**METANITRANILINE**, in combination with copper, yields a fine cutch brown resembling Dianisidine blue and Paranitraniline brown in fastness.

**PHENETIDINE RED or BLUE RED (M.L.B.)**, which is employed principally for pinks, is produced from *o* nitrophenetidine (p. 686) and beta-naphthol.

The other insoluble azo-colours are also only used in calico-printing. We may briefly mention:—

*Aminoazobenzene* with beta-naphthol yields a fine bluish-red fast to washing, but not to light or rubbing. *Aminoazotoluene* with beta-naphthol yields a full garnet colour fast to washing, which, by treatment with copper, becomes very fast to light without being much altered in shade. *Benzidine* and *tolidine* with beta-naphthol produce very full browns, which, however, do not level well, and are not fast to light. *Para brown* is the name given by M.L.B. to a brown obtained by preparing with Chrysoidine in place of beta-naphthol and developing in diazotised *p* nitraniline.

The production of insoluble azo-blacks has not yet been very successful, and is used to a moderate extent only in calico-printing. **AZO-BLACK BASE O (M.L.B.)** is a mixture of bases, which is also furnished in the form of a stable diazo-compound named **AZOPHOR BLACK S (M.L.B.)**, and yields reddish-black on beta-naphthol prepare. **AMINOCHRYSOÏDINE**, marketed as **AZOTOL C (Cassella)** or **PRAGUE ICE BLACK (Kinzelberger & Co. in Prague)**, also produces a reddish-black with beta-naphthol. Brownish-blacks are obtained with diazotised *p* nitraniline on **AMIDONAPHTHOL B D and 3 B (Cassella)**. Diazotised benzidine yields a good black on **ICE BLACK B S (Bayer)**—*i.e.*, 2 : 3 dioxynaphthalene 6 sulphonic acid.

H. Koechlin\* has described several colours which he has prepared on piece goods, which, however, have not found much application.

The cotton pieces are first padded with a solution of 25 parts of beta-naphthol in 25 parts of caustic soda, 100° Tw. (46 per cent. NaOH), and 100 parts of water. After drying, the prepared goods are passed for half a minute through a diazotising bath. A bath for blue is prepared with 100 parts of Safranine dissolved in 75 parts of hydrochloric acid and 1,000 parts of water, and, further, with 20 parts of sodium nitrite, 125 parts of water, and 250 of

\* *Journ. Soc. Dyers and Col.*, 1890, p. 152.

ice, to which are added, lastly, 250 parts of sodium acetate and 1,000 parts of water. The blue is not very brilliant, and not fast to light.\*

Kalle & Co.† have taken out a patent in Germany for producing yellow to brown colours on cotton by first mordanting with tannin, catechu, &c., and then passing through a diazo-solution.

According to E. C. Kayser, the diazo-compounds are fixed by the salts of tannic acid without producing azo-compounds with the latter, and may subsequently be coupled with phenols. Thus cotton can be mordanted with tannin and antimony as for basic colours, then treated in a diazo-solution, and finally in beta-naphthol solution. This process would offer the advantage that the diazo and naphthol liquors are well exhausted, but it does not find any practical application. M. Goldovsky has proposed to treat the animal fibres in a diazo-solution and to develop, subsequently, in naphthol solution. But this process also is not employed in practice.‡

#### ADDENDUM.

##### NITROSO BLUE (M.L.B.).

This blue is also produced on the fibre with the aid of phenols; no diazo-compounds, however, are used, the bases being directly condensed on the fibre with the phenols so as to form oxazine compounds, identical with, or analogous to, New blue (p. 486). Cotton cloth is padded with an alkaline solution of beta-naphthol, dioxynaphthalene, resorcin, &c., dried, and printed with a printing colour containing nitrosodimethylaniline (or a similar base) and tannic acid in acetic acid solution. After steaming two to three minutes in a rapid ager, the tissue is passed through the solution of an antimony salt, washed, and soaped. Or the cloth is padded in a mixture of the phenolic compound, base, and tannic acid, steamed as before, and passed through an antimony bath. This very interesting process is, however, only used in calico-printing.

#### COMPOUNDS OF THE AROMATIC SERIES.

Phenol (*Carbolic Acid*),  $C_6H_4(OH)$ , occurs in coal tar. It forms, in the pure state, a colourless crystalline mass, which becomes gradually reddish, and is deliquescent in the air; it melts at  $42^\circ C.$  and boils at  $183^\circ$ ; the specific gravity is 1.084 at  $0^\circ$ . It possesses a peculiar smell and a burning taste, is very poisonous, and is antiseptic. It dissolves in 15 parts of water at  $20^\circ$ ; and very freely in alcohol, ether, and glacial acetic acid. The neutral solutions of phenol are coloured violet by ferric salts; bromine water precipitates tribromophenol from solutions, even when highly diluted. Phenol forms salts with metallic bases, such as sodium phenolate ( $C_6H_5ONa$ ); the salts are decomposed by the weakest acids, even by carbonic acid. Phenol dissolves readily in caustic soda, forming the phenolate or phenate of soda.

*Cresol* or *Oxytoluene*,  $C_6H_4(CH_3)(OH)$ .—Ortho-, meta-, and para-cresol are known, and are constituents of crude carbolic acid.

*Resorcin*, or *Metadihydroxybenzene*,  $C_6H_4(OH)_2$ ; ( $OH = 1 : 3$ ), forms colourless crystals, easily soluble in water, alcohol, ether, and in alkalis. It is extensively used for the manufacture of dyestuffs, especially for the Eosins and Rhodamines, and also serves as a developer of diazotised dyestuffs (p. 382).

\* A blue may also be produced, according to Fischesser & Pokorny (*Journ. Soc. Dyers and Col.*, 1892, p. 42), by padding first in an alkaline solution of beta-oxynaphtholic acid (melting point,  $216^\circ$ ), and developing in diazotised dianisidine.

† German Patent, 55,837; *Journ. Soc. Dyers and Col.*, 1891, p. 147

‡ *Journ. Soc. Dyers and Col.*, 1897, p. 150.

**Alpha-naphthol**,  $C_{10}H_7(OH)$ ; (OH : 1), is obtained from naphthalene by fusing alpha-naphthalene monosulphonic acid with caustic soda. It crystallises in colourless, glittering needles, melts at  $95^\circ C.$ , boils at  $278^\circ$  to  $280^\circ$ , and has a phenolic smell. It is sparingly soluble in hot water, freely in alcohol and ether. Ferric chloride produces a violet precipitate in the aqueous solution. Alpha-naphthol, like phenol, forms salts (*naphtholates*), and dissolves in caustic soda.

**Beta-naphthol**,  $C_{10}H_7(OH)$ ; (OH : 2), is obtained analogously to alpha-naphthol by fusing beta-naphthalene monosulphonic acid with caustic soda. It crystallises in colourless, glittering laminae, melts at  $122^\circ C.$ , and boils at  $286^\circ$ . It is sparingly soluble in hot water, readily in alcohol and ether. The aqueous solution becomes greenish on addition of ferric chloride. Beta-naphthol also resembles the phenols in forming salts (*naphtholates*), and dissolves in caustic soda.

The *azo-compounds* of beta-naphthol are essentially different from those of alpha-naphthol. They possess in the non-sulphonated state a slightly basic character, and apparently contain no hydroxyl group, not being soluble in caustic soda.

*Dioxy-naphthalenes*,  $C_{10}H_6(OH)_2$ .—A great number of these are known, several of which are very important for the manufacture of colouring matters.

**Aniline** (*Amino-Benzene*),  $C_6H_5NH_2$ .—Aniline was discovered in 1826, by Unverdorben; he obtained it by the dry distillation of indigo and called it *crystalline*. Previously Hellot had observed the formation of aniline in a similar way.\* Runge found it in 1834 in coal tar and named it *kyanol*. Zinin prepared it first from nitrobenzene in 1842, and described it as *benzidame*. The name *aniline* (from *añil*, Span. = indigo) was proposed by Fritsche, who prepared it in 1840 from indigo by means of caustic potash. A. W. Hofmann found in 1843 that the various products were identical. Aniline was manufactured on the large scale only after Perkin's discovery of Mauve in 1856.

For the production of aniline, benzene is converted into nitrobenzene ( $C_6H_5NO_2$ ) by treatment with a mixture of nitric and sulphuric acids; and the product is reduced with hydrochloric acid and iron.

Aniline is a colourless oil having a peculiar smell and a strong power of refracting light. It soon becomes brown under the influence of light and air. It solidifies in a freezing mixture and melts again at  $-8^\circ C.$ , boils at  $182^\circ$ ; it volatilises freely with steam. The specific gravity is 1.0265 at  $15^\circ$ , 1.024 at  $17.5^\circ$ , and 1.0195 at  $20^\circ$  (for practical calculations = 1).

One part of aniline is soluble in 31 parts of water at  $12.5^\circ$ ; it dissolves in all proportions in a 50 per cent. solution of aniline hydrochloride in water, and aniline hydrochloride generally increases the solubility of aniline in water. Aniline is readily soluble in most of the usual solvents and is itself a good solvent for many substances, such as sulphur, phosphorus, indigo, aniline blue, and camphor, but not for caoutchouc. It burns with a smoky flame. It possesses a feeble, characteristic smell and burning taste. The vapours of aniline are very poisonous, when inhaled, and produce peculiar and distressing symptoms, the so-called *anilisme*, frequently occurring in aniline works and in aniline black dye-houses. Aniline poisoning may also result from contact with the skin of aniline oil or solutions of aniline salt. The oil when taken internally is very poisonous.†

\* *Journ. Soc. Dyers and Col.*, 1898, p. 162.

† In order to prevent aniline poisoning the working rooms should be well ventilated and men not very sensitive to aniline should be employed, but even these should not work continuously with aniline. If the clothing or overalls have had aniline oil spilt on them, they should be taken off immediately, as the aniline oil evaporating from the clothing is also very dangerous. People who have suffered from anilisme remain very sensitive to aniline.

Aniline is a monacid base and forms well crystallised salts. It is readily affected by chemical agents and undergoes many changes by oxidation under different conditions which are very important in the production of dyestuffs and in dyeing.

*Commercial aniline.*—The purest product is *aniline for blue*, which consists of almost pure aniline. The other brands, such as “aniline for red,” contain varying quantities of homologous bases, chiefly ortho- and paratoluidine.

Aniline and its hydrochloride are used by dyers chiefly for the production of aniline black.

*Aniline hydrochloride*,  $C_6H_5NH_2 \cdot HCl$ , is the most important salt of aniline, and is sold in large quantities under the name *aniline salt*. It crystallises in large leaf-shaped white crystals which become coloured in the air from grey to black; it is freely soluble in water and in alcohol, melts at  $192^\circ$ , and volatilises without decomposition.

*Aniline sulphate*,  $(C_6H_5NH_2)_2 \cdot H_2SO_4$ , is sparingly soluble in water and in alcohol, but insoluble in ether. An unstable acid sulphate  $(C_6H_5NH_2 \cdot H_2SO_4)$  has also been prepared.

*Aniline hydrofluoride*,  $C_6H_5NH_2 \cdot HF$ , is marketed as *aniline fluoride* (Bayer) in the form of a greenish paste.

*Toluidines*,  $C_6H_4(CH_3)NH_2$ .—Three isomeric toluidines are known, which strongly resemble aniline; they are obtained by the reduction of three different nitrotoluenes. By the action of nitric acid on toluene, chiefly ortho- and paranitrotoluene are obtained, which yield on reduction a mixture of ortho- and paratoluidine.

*Orthotoluidine* is a colourless oil which boils at  $197^\circ$  to  $197.5^\circ$  C. and has a specific gravity of 1.0037 at  $15^\circ$ .

*Metatoluidine* is a colourless oil which boils at  $197^\circ$  C. It occurs in small quantities only in the commercial products and has no practical value owing to its high cost.

*Paratoluidine* forms colourless crystals, which melt at  $45^\circ$  C. and boil at  $198^\circ$ .

*Xylidine*,  $C_6H_3(CH_3)_2NH_2$ .—The commercial article is a mixture of isomeric compounds, and chiefly contains *m* xylidine (amino *m* xylene,  $CH_3$ : 1 and 3,  $NH_2$ : 4), *p* xylidine (amino *p* xylene,  $CH_3$ : 1 and 4,  $NH_2$ : 2), &c. *m* xylidine is also employed in the pure state.

*Cumidine*,  $C_6H_2(CH_3)_3NH_2$ .

*Nitraniline*,  $C_6H_4(NO_2)NH_2$ . Of the three isomeric compounds the paranitraniline is the most important, and especially so in the form of its diazo-compound for the production of azo-colours on the fibre and for coupling certain direct cotton colours (see pp. 383 and 678).

*Nitrotoluidine*,  $CH_3C_6H_3(NO_2)NH_2$ .

*Anisidine*,  $C_6H_4(O \cdot CH_3)NH_2$ .

*Phenetidine*,  $C_6H_4(O \cdot C_2H_5)NH_2$ .

*Nitrophenetidine*,  $C_6H_3(O \cdot C_2H_5)(NO_2)NH_2$ , see p. 683.

*Phenylenediamine*,  $C_6H_4(NH_2)_2$ .

*Metatolylenediamine*,  $OH_2 \cdot C_6H_3(NH_2)_2 \cdot (OH_3 : 1, NH_2 : 2 \text{ and } 4)$ , see p. 383.

*Benzidine*,  $H_2N \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$ .

Benzidine or di *p* aminodiphenyl forms large colourless silky plates, melting at  $122^\circ$  C. Its sulphate is sparingly soluble in water, the hydrochloride is readily soluble. By the action of nitrous acid it is converted into salts of tetrazodiphenyl which combine with the sulphonic acids or amines to form azo-colours dyeing unmordanted cotton from an alkaline bath. Benzidine, therefore, may be considered as the fundamental base of the direct cotton colours.

An insoluble azo-colour is formed on the cotton fibre with the aid of tetrazo-diphenylchloride and beta-naphthol (see p. 683).

Tolidine,  $H_2N \cdot C_7H_6 \cdot C_7H_6 \cdot NH_2$ , or di *p* aminoditolyl is the next homologous compound, corresponding to benzidine. It melts at  $128^\circ C$ . and also forms a sparingly soluble sulphate. It is of equal importance for the production of colouring matters, and is also used for developing insoluble azo-colours on the cotton fibre (see p. 683).

Ethoxybenzidine or di *p* aminoethoxydiphenyl,  
 $H_2N \cdot C_6H_4 \cdot C_6H_3(O \cdot C_2H_5) \cdot NH_2$ .

Dianisidine or di *p* amino di methoxydiphenyl,  
 $H_2N \cdot C_6H_3(O \cdot OH_3) \cdot C_6H_3(O \cdot CH_3)NH_2$ .

These two bases are also very important for the production of direct cotton colours, and dianisidine in addition serves for the production of Dianisidine blue (see p. 682).

Aminoazobenzene,  $C_6H_5 \cdot N : N \cdot C_6H_4NH_2$ .

Aminoazotoluene,  $C_7H_7 \cdot N : N \cdot C_7H_5 \cdot NH_2$ .

These two bases are very important for the manufacture of azo-colours, and also serve for the production of insoluble azo-colours on the cotton fibre.

Ethyl Beta-naphthylamine,  $C_{10}H_7NH \cdot C_2H_5$ , is known as claret developer or Developer B (p. 383).

Naphthylamine ether or aminonaphthol ether,  $\beta C_{10}H_6(NH_2)(O \cdot C_2H_5)$  is also used as a developer (p. 383).

Dehydrothio *p* toluidine,  $C_7H_6 < \underset{S}{N} > C \cdot C_6H_4 \cdot NH_2$ .

Primuline base,  $C_7H_6 < \underset{S}{N} > C \cdot C_6H_3 < \underset{S}{N} > C \cdot C_6H_3 < \underset{S}{N} > C \cdot C_6H_4 \cdot NH_2$ .

Dehydrothiotoluidine and Primuline base are produced by strongly heating *p* toluidine with sulphur (see also *Primuline*, p. 409).

Dehydrothioxylidine,  $C_8H_8 < \underset{S}{N} > C \cdot C_7H_6 \cdot NH_2$ , is formed analogously to dehydrothiotoluidine by heating xylidine with sulphur.

Alpha-naphthylamine,  $C_{10}H_7NH_2$ ; ( $NH_2 : 1$ ), is obtained by reducing alpha-nitronaphthalene, the product of the reaction of nitric acid on naphthalene. It forms colourless crystals, which melt at  $50^\circ C$ ., and boils at  $300^\circ$ . It is almost insoluble in water, but freely soluble in alcohol or ether. The commercial product has a reddish-grey to brown colour and a very disagreeable smell. It should dissolve in hot diluted acids without leaving much insoluble oil. Mild oxidising agents produce a blue precipitate in the solutions of alpha-naphthylamine salts. Alpha-naphthylamine resembles aniline chemically. It is a monacid base and forms crystalline salts which are not very soluble in water.

Beta-naphthylamine,  $C_{10}H_7NH_2$ ; ( $NH_2 : 2$ ), is prepared by heating beta-naphthol with ammonia. It forms colourless inodorous laminae, melts at  $112^\circ$  and boils at  $294^\circ$ . It is sparingly soluble in cold but freely soluble in hot water, alcohol, and ether. The commercial product is very pure and forms a fused pink-coloured mass. Beta-naphthylamine is a monacid base and forms crystalline salts. The hydrochloride ( $C_{10}H_7NH_2 \cdot HCl$ ) is fairly soluble in water.

**Sulphonic Acids.**—The constitution of a number of sulphonic acids mentioned in the description of the dyestuffs is indicated below.

*Alpha-naphthol sulphonic acid (NW)*,  $(C_{10}H_6)(OH)(SO_3H)$ , (1 : 4), is obtained from naphthionic acid, and was first prepared by Neville and Winther.

*Alpha-naphthol sulphonic acid Cl or L*,  $(C_{10}H_6)(OH)(SO_3H)$ , (1 : 5), is the compound obtained from alpha-naphthylamine sulphonic acid (L) (see below).

*Alpha-naphthol disulphonic acid (Sch.)*,  $C_{10}H_5(OH)(SO_3H)_2$ ; (OH : 1,



$\text{SO}_3\text{H}$  : 4 and 8), was discovered by Mensching and patented by the Schoellkoff Aniline Co.

*Alpha-naphthol epsilon-disulphonic acid*,  $\text{C}_{10}\text{H}_5(\text{OH})(\text{SO}_3\text{H})_2$ ; ( $\text{OH}$  : 1;  $\text{SO}_3\text{H}$  : 3 and 8), was discovered by Andresen and patented by the Berlin Aniline Co.

*Alpha-naphthol disulphonic acid R G*,  $\text{C}_{10}\text{H}_5(\text{OH})(\text{SO}_3\text{H})_2$ ; ( $\text{OH}$  : 1,  $\text{SO}_3\text{H}$  : 3 and 6), was discovered by Rudolph and Gürke.

*Beta-naphthol (mono) sulphonic acid (S)*,  $\text{C}_{10}\text{H}_6(\text{OH})(\text{SO}_3\text{H})$ ; (2 : 6), was discovered by Schaeffer and is known as Schaeffer's acid.

*Beta-naphthol (mono) sulphonic acid (B)*, or beta-naphthol alpha-sulphonic acid,  $\text{C}_{10}\text{H}_6(\text{OH})(\text{SO}_3\text{H})$ ; (2 : 8), was discovered by Rumpf and patented by the Elberfeld Colour Works (Bayer).

*Beta-naphthol (mono) sulphonic acid (F)*,  $\text{C}_{10}\text{H}_6(\text{OH})(\text{SO}_3\text{H})$ ; (2 : 7), the so-called "F acid," was patented by L. Cassella & Co.

*Beta-naphthol disulphonic acid R (R. salt)*,  $\text{C}_{10}\text{H}_5(\text{OH})(\text{SO}_3\text{H})_2$ ; ( $\text{OH}$  : 2,  $\text{SO}_3\text{H}$  : 3 and 6), was discovered by Baum and patented by M.L.B.

*Beta-naphthol disulphonic acid G (G Salt; Gamma acid)*,  $\text{C}_{10}\text{H}_5(\text{OH})(\text{SO}_3\text{H})_2$ ; ( $\text{OH}$  : 2,  $\text{SO}_3\text{H}$  : 6 and 8), was patented by the Hoechst Colour Works (M.L.B.). *N.B.*—The gamma-aminonaphthol sulphonic acid, prepared from this acid (see below), is also frequently called Gamma acid; in this book the term, however, always signifies the beta-naphthol disulphonic acid.

*Beta-naphthol delta-disulphonic acid*,  $\text{C}_{10}\text{H}_5(\text{OH})(\text{SO}_3\text{H})_2$ ; ( $\text{OH}$  : 2;  $\text{SO}_3\text{H}$  : 3 and 7), is obtained from "F acid" and was patented by L. Cassella & Co.

*1 : 8 Dioxynaphthalene 4 sulphonic acid S*,  $\text{C}_{10}\text{H}_5(\text{OH})_2(\text{SO}_3\text{H})$ ; ( $\text{OH}$  : 1 and 8,  $\text{SO}_3\text{H}$  : 4), is produced by melting alpha-naphthol disulphonic acid S with caustic soda.

*1 : 8 Dioxynaphthalene 3 : 6 disulphonic acid*,  $\text{C}_{10}\text{H}_4(\text{OH})_2(\text{SO}_3\text{H})_2$ ; ( $\text{OH}$  : 1 and 8,  $\text{SO}_3\text{H}$  : 3 and 6), is the so-called Chromotropic acid of the Hoechst Farbwerke, the sodium salt of which is marketed under the name of Chromogene I (M.L.B.).

*1 : 8 Dioxynaphthalene 4 : 6 sulphonic acid K*,  $\text{C}_{10}\text{H}_4(\text{OH})_2(\text{SO}_3\text{H})_2$ ; ( $\text{OH}$  : 1 and 8,  $\text{SO}_3\text{H}$  : 4 and 6).

*Sulphanilic acid* or *paramino benzene sulphonic acid*,  $\text{C}_6\text{H}_4(\text{NH}_2)\text{SO}_3\text{H}$ .

*Metanilic acid* or *meta-amino benzene sulphonic acid*,  $\text{C}_6\text{H}_4(\text{NH}_2)\text{SO}_3\text{H}$ .

*Diaminostilbene disulphonic acid*,  $\text{H}_2\text{N} > \text{C}_6\text{H}_3 - \text{CH} = \text{CH} - \text{C}_6\text{H}_3 < \text{NH}_2$   
 $\text{HO}_2\text{S}$   $\text{SO}_3\text{H}$

*Naphthionic acid*,  $\text{C}_{10}\text{H}_6(\text{NH}_2)(\text{SO}_3\text{H})$ ; (1 : 4), is the alpha-sulphonic acid of alpha-naphthylamine discovered by Piria, which is prepared by heating alpha-naphthylamine sulphate (Neville and Winther).

*Alpha-naphthylamine sulphonic acid (L)*,  $\text{C}_{10}\text{H}_6(\text{NH}_2)(\text{SO}_3\text{H})$ ; (1 : 5), was discovered by Laurent.

*Alpha-naphthylamine sulphonic acids (Clève)*. According to Clève, three sulphonic acids are produced by nitrating and subsequently reducing beta-naphthalene sulphonic acid—viz.,  $\text{C}_{10}\text{H}_6(\text{NH}_2)(\text{SO}_3\text{H})$ ; ( $\text{NH}_2$  : 1,  $\text{SO}_3\text{H}$  : 3 or 6 or 7).

*Alpha-naphthylamine disulphonic acid*,  $\text{C}_{10}\text{H}_5(\text{NH}_2)(\text{SO}_3\text{H})_2$ . Various acids of this composition are known, which are produced either by reducing alpha-nitronaphthalene disulphonic acids, or by sulphonating alpha-naphthylamine monosulphonic acids. Alpha-naphthylamine disulphonic acid D is a mixture of the two acids,  $\text{NH}_2$  : 1,  $\text{SO}_3\text{H}$  : 4 and 6, or 4 and 7.

*Beta-naphthylamine alpha-sulphonic acid*,  $\text{C}_{10}\text{H}_6(\text{NH}_2)(\text{SO}_3\text{H})$ ; (2 : 8), was patented by the Badische Anilin- und Soda-Fabrik (B.A.S.F.).

*Beta-naphthylamine beta-sulphonic acid*, or *beta-naphthylamine sulphonic acid (Br.)*,  $\text{C}_{10}\text{H}_6(\text{NH}_2)(\text{SO}_3\text{H})$ ; (2 : 6), was discovered by Prinz and patented by Broenner's Colour Works.

*Beta-naphthylamine gamma-sulphonic acid*, or *beta-naphthylamine sulphonic acid (D)*,  $C_{10}H_6(NH_2)(SO_3H)$ ; (2 : 5), was patented by Dahl & Co.

*Beta-naphthylamine delta-sulphonic acid*, or *beta-naphthylamine sulphonic acid (F)*, or *delta-acid*,  $C_{10}H_6(NH_2)(SO_3H)$ ; (2 : 7).

*Methylnaphthylamine delta-sulphonic acid*,  $C_{10}H_6(NH \cdot CH_3)(SO_3H)$ ; (NH  $\cdot$  CH<sub>3</sub> : 2, SO<sub>3</sub>H : 7).

*Beta-naphthylamine disulphonic acid (R)*,  $C_{10}H_6(NH_2)(SO_3H)_2$ ; (NH<sub>2</sub> : 2, SO<sub>3</sub>H : 3 and 6) (*amino R acid*), is produced by the action of ammonia on R salt.

*Beta-naphthylamine disulphonic acid (G)*,  $C_{10}H_5(NH_2)(SO_3H)_2$ ; (NH<sub>2</sub> : 2, SO<sub>3</sub>H : 6 and 8) (*amino G acid*), is produced by the action of ammonia on G salt.

*Gamma-aminonaphthol sulphonic acid*,  $C_{10}H_5(NH_2)(OH)(SO_3H)$ ; (NH<sub>2</sub> : 2, OH : 8, SO<sub>3</sub>H : 6), is produced by heating amino G acid with caustic soda.

*Aminonaphthol sulphonic acid S*,  $C_{10}H_5(NH_2)(OH)(SO_3H)$ ; (OH : 1, SO<sub>3</sub>H : 5, NH<sub>2</sub> : 8).

*Aminonaphthol disulphonic acid SS*,  $C_{10}H_4(NH_2)(OH)(SO_3H)_2$ ; (OH : 1, SO<sub>3</sub>H : 5 and 7, NH<sub>2</sub> : 8).

*Aminonaphthol disulphonic acid H*,  $C_{10}H_4(OH)(NH_2)(SO_3H)_2$ ; (OH : 1, SO<sub>3</sub>H : 3 and 6, NH<sub>2</sub> : 8).

*Aminonaphthol disulphonic acid K*,  $C_{10}H_4(OH)(NH_2)(SO_3H)_2$ ; (OH : 1, SO<sub>3</sub>H : 3 and 5, NH<sub>2</sub> : 8).

## PART VIII.

## MINERAL COLOURS.

THE mineral colours have lost much of their former importance since the discovery of the aniline colours. They are nevertheless still largely employed on account of their fastness and the low cost of their production. The mineral colours are totally different from the natural and artificial organic colouring matters both in their general chemical characters and in their tinctorial properties and methods of application.

The mineral colours which are now used to any considerable extent in dyeing are the following:—

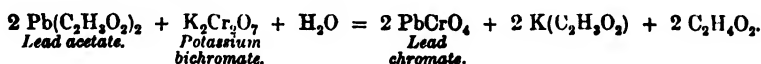
- |                     |                                 |
|---------------------|---------------------------------|
| 1. Chrome yellow.   | 5. Iron-buff and Nankin yellow. |
| 2. Chrome orange.   | 6. Khaki.                       |
| 3. Chrome green.    | 7. Prussian blue.               |
| 4. Manganese brown. |                                 |

Several other mineral substances are used as pigments in calico-printing.

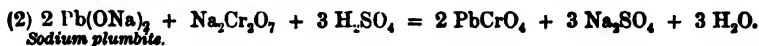
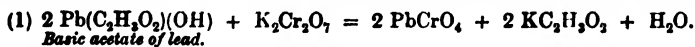
We shall here describe only those colours which are still important for the dyeing proper of the textile fibres.

**CHROME YELLOW** or **CHROMATE OF LEAD**,  $\text{PbCrO}_4$ .

Chromate of lead occurs native, and is manufactured in large quantities as a pigment by precipitating the solution of a lead salt (acetate or nitrate of lead) with bichromate of potassium or sodium :



The compound can also be produced from a basic lead salt or from an alkaline plumbite (compound of lead hydroxide and an alkali) (see p. 286).



Chrome yellow forms an orange-yellow powder, and is quite insoluble in water and other neutral solvents, but dissolves readily in nitric acid and in caustic potash or soda; the latter agents, however, convert it first into a basic lead chromate. (See *Chrome orange*.)

Chromate of lead is used as an oxidising agent in the laboratory, and has also been recommended as such for the production of Aniline black by oxidising the aniline in the fibre.

Chrome yellow is produced in dyeing by first impregnating the fibre with a lead salt, and then passing the material through a solution of a bichromate. The processes are precisely similar to those which occur in mordanting and dyeing with the mordant colours; the lead salt plays the rôle of the mordant and the

bichromate acts as the dyestuff. The analogy goes still further, inasmuch as the dyestuff possesses a distinct chromophor "Cr," and—in the form of free chromic acid,  $H_2CrO_4$ —the auxochromous group (OH). Finally, lead is not the only mordant for the bichromate dyestuff, although by far the best, since soluble barium salts produce a similar Chrome yellow.

*Application.*—Chrome yellow is dyed on cotton only. The colour varies from a light lemon-yellow to a full orange-yellow, and is distinguished by almost absolute fastness to light, soap, and acids; by alkalies it is turned orange (see below); by sulphuretted hydrogen it becomes brownish, lead sulphide being formed. To produce the colour the cotton is impregnated with nitrate or acetate of lead, and after precipitation of the lead in the fibre, as oxide or sulphate (by means of ammonia, lime, or sodium sulphate), is passed through a dilute solution of potassium bichromate. Another method is to impregnate the material with a plumbite and then to pass it through an acidulated solution of bichromate.

*First Method.*—A basic salt is used in order to save the expense of acid as also to precipitate more lead in the fibre.

*Preparing of Stock Liquor.*—Dissolve, boiling, 100 kgs. (100 lbs.) of brown-sugar of lead and 50 kgs. (50 lbs.) of litharge in 360 litres (16 galls.) of water and allow to settle; the liquor should stand at 125° Tw.

*Dyeing.*—Pass the yarn through lime-water (1½° Tw.) and wring; then work in a solution of basic lead salt prepared by diluting stock liquor with cold water to 10° Tw., wring out and pass through another tub with lime-water (1½° Tw.). The lead liquor is used continuously and maintained at the same strength by the addition of fresh stock liquor. The chrome-bath is prepared with about 6 grms. of bichromate of soda per litre (6 lbs. for 100 galls.)—dissolved in water—and from time to time freshened up with fresh bichromate solution. The yarn is passed through the chrome-bath and then turned a few times in water (containing 1 part of hydrochloric acid for 300 parts of water), finally washed in water and dried.

*Second Method (Lemon-yellow).*—Prepare a stock liquor by dissolving 100 kgs. (100 lbs.) of brown sugar of lead in 800 litres (80 galls.) of water to stand at about 16° Tw. Fill a vat holding 200 litres (40 galls.) with water and add 1½ litres (3 pints) of stock liquor and 5 litres (1 gall.) of caustic soda lye (71° Tw. = 32 per cent. NaOH), turn the yarn about three times in the bath, wring and pass through the chrome-bath, wring, wash, and dry. The chrome-bath is prepared for a vat of 200 litres (40 galls.) with 1½ kgs. (3 lbs.) of bichromate of soda and 200 grms. (6 ozs.) of sulphate of zinc. Both vats are used continuously, and are regularly freshened up; for restoring the strength of the chrome-liquor a solution may be kept of 10 parts of chromate and 1½ parts of sulphate of zinc in a sufficiency of water.

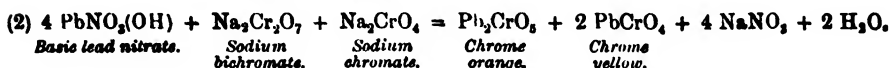
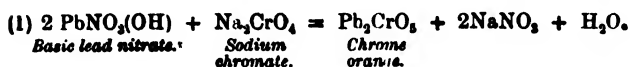
The depth of the ultimate shade obtained by either method is mainly dependent on the strength of the lead solution, and on the quantity of lead oxide which is deposited in the fibre.

The yarn is very heavily weighted by the dyeing with Chrome yellow—even more than 40 per cent.—and to this fact the extensive use of Chrome yellow at the present time is due. Chrome yellow must be considered to be a poisonous dyestuff, as it cannot be denied that the dust of the colour which is rubbed from the materials is injurious to the health of the work-people who pack or handle the dry yarn (as in weaving, embroidering, &c.). Various other dyestuffs of easier application are now in the market which might advantageously replace Chrome yellow; for instance, the yellows of the direct cotton colours.

#### CHROME ORANGE.

Chrome yellow consists of a mixture of normal lead chromate (chrome

yellow) and basic lead chromate,  $\text{Pb}_2\text{CrO}_5$ . It is also used as a pigment. It is produced by precipitating the solution of a basic lead salt with sodium bichromate or chromate; the colour appears the redder the more alkaline the mixture is—i.e., the less Chrome yellow the ultimate colour contains.



Chrome yellow may be converted into Chrome orange by the action of alkalies or limewater; it is in this way that Chrome orange is produced in dyeing.

Chrome orange forms an orange to red powder; it resembles Chrome yellow in its chemical properties.

*Application.*—Chrome orange is produced in dyeing, as stated above, by the action of alkalies on Chrome yellow which has been previously fixed on the fibre by any of the usual methods. For this purpose the yarn is dyed with Chrome yellow, washed in water, and then passed through boiling clear dilute limewater; the cotton must be removed from the limewater bath as soon as the full orange colour is developed, otherwise the colour loses brilliancy, or may be completely stripped; after this the material is washed and dried.

A *three-dip orange* is produced by the first method for Chrome yellow, but in the following order:—(1) Lime-bath, (2) lead-bath, (3) lime-bath, (4) lead-bath, (5) chrome-bath, (6) lead-bath, (7) chrome-bath, and, finally, (8) boiling lime-bath for “raising” the orange.

Chrome orange is a full red-orange colour which equals Chrome yellow in fastness, except that it is fast to alkalies, but is affected by acids. The remarks made on the poisonous action and weighting effect of Chrome yellow also hold good for Chrome orange.

#### CHROME GREEN.

Chrome green, as ordinarily understood in the dyeing trade, is the bright green obtained by topping an indigo blue (usually a light shade) with chrome yellow.

The term is, however, also applied to chromium hydroxide, which has been described in the chapter on mordants (pp. 240 and 251, &c.). The hydroxide yields a very light shade of sea-green, hardly visible in artificial light, and rarely used now. In former years a *chromium arsenite* was produced on the fibre by mordanting with a chromium salt, and then passing through a hot solution of arsenic (arsenite of soda). This process yields a moderately full and very fast green, which does not appear very different when seen by daylight or by artificial light; but its poisonous character renders its use objectionable. Phosphate and silicate of soda have similar effects, but give inferior results. Chromium oxide can be produced on cotton by the usual mordanting methods, and on wool by mordanting the fibre with bichromate, and then passing the material through sodium bisulphite; by repeating the processes or increasing the strength of the bichromate fuller colours are obtained.

A recent process patented by L Cassella & Co. (English Patent 12,831 of 1907), recommends the staining of wool to be used for melanges with metallic oxides. A drab shade, for instance, is produced by boiling wool with 2 per cent. bichromate, 2 per cent. copper sulphate, and 3 per cent. formic acid. When wool stained in this way is mixed with wool dyed a dark shade, the melange obtained is faster to light than with wool stained with organic dye-stuffs or with white wool.

**KHAKI.**

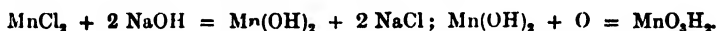
This term, which is of Indian origin, is applied to a peculiar shade of drab, which is largely used for military cloth and other material. The fastest khaki obtained on cotton was originally brought out by Gatti, of Accrington, and is obtained by fixing on the fibre a mixture of chromic and ferric hydrates. The scoured cloth is passed through a mixture of ferrous and chromic acetates (the latter being obtained by the reduction of bichromate with glucose and sulphuric acid in presence of acetic acid) which stands at 36° Tw., being given two dips in the padding machine, after which it is dried on wrapped tins. After drying, the cloth is steamed for four minutes in a rapid ager in which the steam and air are maintained at a temperature of 220° F. The goods are then passed through a boiling solution of caustic soda and sodium carbonate, standing at 12° Tw. The proportion of caustic soda to sodium carbonate in the fixing liquor is 1 : 3. A mineral khaki contains from 5 to 7 per cent. ash.

Light shades of khaki may also be obtained, according to J. J. Hummel, on cotton yarn or cloth by first mordanting with tannin, fixing the tannin with iron, and then chroming with bichromate. The latter destroys the tannic acid, and a mixture of ferric and chromic hydrates is thrown down on the fibre.

A well dyed mineral khaki is one of the fastest colours known, but possesses a disadvantage inasmuch as the large amount of metallic hydrates, which it is necessary to deposit in the fibre in order to obtain the desired shade, renders the material rather stiff and difficult to penetrate with a needle. By imitating the shade with sulphide colours, this drawback may be overcome, but the resultant shades though sufficiently fast for the generality of purposes are not equal in fastness to the mineral khaki. Very fast shades of khaki can be produced on cotton by means of the Indanthrene colours, but, as yet, this means of obtaining the shade appears to be too expensive.

**MANGANESE BROWN or MANGANESE BRONZE (BISTRE).**

Manganese brown is produced by precipitating manganous hydroxide in the fibre, and then oxidising this compound with the aid of atmospheric oxygen or such oxidising agents as chloride of lime:—



Manganese brown is probably a hydrate of the peroxide,  $\text{MnO}_2$ , but containing less water than the compound,  $\text{MnO}_2 \cdot \text{H}_2\text{O}$ .

*Application.*—Manganese brown is dyed on the cotton fibre, and produces a full neutral brown, which is almost absolutely fast to light, soap, dilute acids, and alkalis. For the production of the colour the solution of manganous chloride, obtained as a bye-product in the manufacture of chloride of lime and known as "bronze liquor," is used, after neutralising any free mineral acid which may be present. The cotton is impregnated with the manganous liquor, and then passed through a hot solution of caustic soda (2° to 3° Tw.). It is important that the caustic soda should be free from sodium carbonate, because that impurity causes manganous carbonate to be precipitated in the fibre, which does not oxidise readily, and is liable to produce an irregular colour; nor should the alkaline liquor be too cold or too dilute, otherwise a manganous hydrate is formed which also does not readily oxidise. The hydrate is at first colourless, but it soon oxidises and becomes brownish. The oxidation by the air, however, is not sufficient to produce a full brown, and a passage through a weak solution of chloride of lime or through a bichromate solution is required to complete the oxidation.

The process is simplified by adding sodium hypochlorite directly to the solution of caustic soda; in this case precipitation and oxidation take place simultaneously.



solutions have a weakening influence on the cotton fibre, especially if the oxidation proceeds rapidly, and this fact must not be lost sight of.

The dyeing process can be repeated for the production of fuller shades.

#### **PRUSSIAN BLUE.**

The chemical properties of Prussian blue have been described in a previous chapter (p. 265). Prussian blue, strictly speaking, is not a mineral colour, since the prussiates, its chief constituents, are organic compounds; the colour consists, however, largely of iron, and is so similar to the metallic compounds that we follow the general custom by describing it among the mineral colours.

Prussian blue may be considered to be a mordant colour produced by the dyestuff "yellow prussiate," on the one hand, and the ferric mordant, on the other; the colour deserves to be called polygenetic, since the prussiates produce various coloured products with most of the metallic oxides; Prussian blue, however, is the only colour which is used in dyeing, printing, or painting.

*Application.*—Prussian blue is produced on the textile fibres by two essentially different methods. The first is to mordant with ferric oxide and to dye with yellow prussiate; it is used for the dyeing of cotton and silk. The second method is based on the decomposition the prussiates undergo with formation of Prussian blue when they are heated in acid solutions; this process is used in woollen dyeing and in textile printing.

Frequently a stannous salt is added either to the iron mordant or to the prussiate to produce a brighter and more purplish tone. The salt probably exerts a reducing action before entering the ultimate compound. Under certain conditions stannic chloride is used. The exact composition of the resulting colours has not yet been ascertained.

Prussian blue is extremely fast to light; it fades somewhat by prolonged exposure to sunlight; but according to Chevreul, the colour is restored if kept for some time in the dark. On wool, the colour turns darker on exposure to light. Alkaline or boiling soap solutions readily decompose Prussian blue, leaving brown ferric oxide on the fibre; acids have no action on the colour. Since the introduction of the Aniline blues, the use of the colour has considerably decreased.

*Cotton.*—To dye Prussian blue on cotton, the material is first dyed iron-buff and then passed through an acidified solution of yellow prussiate of potash (or soda); the depth of colour depends on the amount of ferric oxide already precipitated in the fibre; the mordanting and dyeing operations can be repeated alternately to produce a fuller shade. Stannous chloride may be added to the mordanting bath, or (for piece goods) the material can be padded first with stannate of soda and then mordanted with nitrate of iron and stannous chloride. The mordanted goods are passed through a cold or lukewarm solution of 2 parts of yellow prussiate and 1 part of sulphuric acid per 100 parts of dye-liquor; they are finally washed in water and dried.

The pigment Prussian blue (see p. 265) is largely employed in the finishing of black and blue velveteens. This finely-ground pigment, mixed with linseed oil, is applied to the face of the dyed fabric by means of circular brushes which distribute it evenly over the surface. The fixation is subsequently effected by ageing for eight to ten hours in a chamber supplied with a current of air and heated to about 120° C.

*Wool.*—The mordanting and dyeing method does not give satisfactory results on wool and is rarely used. Prussian blue is produced on this fibre without previous mordanting with iron, by decomposition of the acidulated solutions of the prussiates. Before treating the wool with the prussiates, it may be mordanted at the boil with stannous chloride and oxalic acid; or it may be dyed directly with the prussiates. Sulphuric, hydrochloric, and nitric acids are used for acidifying; nitric acid gives the best results with yellow prussiate, probably



on account of its oxidising action—about equal quantities of yellow prussiate and of nitric acid (64° Tw.) are used. Nitric acid also makes the colour greener. Generally speaking, sulphuric acid is most satisfactory. Mixtures also of the three acids are used; for instance, 4 measures of sulphuric acid, 2 measures of hydrochloric acid (32° Tw.), and 1 to 2 measures of nitric acid (64 Tw.). The wool is introduced into a cold bath containing about 10 per cent. of yellow prussiate and 20 per cent. of sulphuric acid, the temperature is raised in the space of one hour to the boiling-point, and the boiling continued for a half to three-quarters of an hour. The colour is rendered brighter and more purplish by adding 1 to 2 per cent. of stannous chloride during the last half or three-quarters of an hour of the boiling. Instead of the stannous chloride, "muriate of tin," or "finishing blue spirits," and similar preparations of stannous salts are used. A process of this kind is still used in some cases for a special kind of goods. The dye-bath is prepared with a cold solution of 12 per cent. red prussiate of potash,  $1\frac{1}{2}$  per cent. of tartar,  $\frac{3}{4}$  per cent. of tartaric acid (of the weight of the goods),  $\frac{1}{2}$  per cent. stannous chloride, and 10 per cent. of Glaubersalt is added. The material is entered at the ordinary temperature. The bath is gradually heated to the boil, and the boiling is continued for 30 to 60 minutes, until the shade is developed. A dark blue is sometimes produced in a similar way, using, however, only one-half that amount of red prussiate and topping afterwards in the same or in a fresh bath with logwood. The colours thus produced may be detected by the reaction with nitric acid which produces green spots on the cloth

During the dyeing of Prussian blue on wool, prussic acid is given off, though not in such quantities as to be actually dangerous.

Silk is now rarely dyed with Prussian blue, except for weighting in black dyeing (see p. 343). The processes which are employed resemble those used for cotton. The silk is first mordanted with ferric oxide, soaped at the boil as described on p. 269 for weighting boiled-off silk, and subsequently dyed with prussiate in an acidulated solution (see p. 270).

A brighter blue, known as "Napoleon's blue," was formerly produced as follows:—The silk is worked for half an hour in a cold bath containing 50 per cent. of basic ferric sulphate (50° Tw.), 10 per cent. of stannous chloride, and 5 per cent. of sulphuric acid; after this, it is wrung out and washed, and then worked for half an hour in another bath, prepared with 10 per cent. of yellow prussiate of potash, 2 to 5 per cent. of red prussiate of potash, and 12 to 15 per cent. of sulphuric acid. The silk is then wrung, and both processes are repeated. Finally, the silk is softened and brightened in a cold bath, prepared with 15 per cent. of olive oil and 5 per cent. of sulphuric acid (of the weight of the silk); wrung and dried.

---

## PART IX.

## MACHINERY USED IN DYEING.\*

THE textile fibres are either dyed in the loose state, in the form of slubbing, tops or sliver (after combing or carding), in the yarn (hank, warp, or cop), or, lastly, in the piece.

By far the largest amount of coloured material which comes into the market is dyed in the piece, because this is at the same time the most convenient and the cheapest method of dyeing, less labour and less materials being required to produce a given shade on the same class of material than by any of the other methods.

The dyeing in the loose state, as slubbing (sliver) or as yarn, is generally done because it is necessary in the production of figured materials containing more than one colour (prints excepted), or of mixed or fancy yarns; but the dyeing is also sometimes done before weaving in the manufacture of high-class goods of *plain* design, in order to produce superior results, especially in woollen piece goods. The dyeing of loose fibre and slubbing is rendered still more expensive to the spinner and manufacturer by the tendency which the fibres have of becoming matted or felted during the process, inasmuch as many of the fibres are subsequently torn in the processes which the dyed material has to undergo preparatory to spinning. The average length of the staple is thus diminished, which, of course, means a loss.

The dyeing of cotton or wool in the loose state, or in the form of sliver or slubbing, is frequently done for the following purpose:—The material is dyed in some dozen to twenty different standard colours, including blacks, blues, reds, greens, yellows, drabs, &c. A stock is kept of each, and the desired shade of yarn is produced in the drawing, previous to spinning by mixing the coloured material with, or without, the addition of undyed material in the requisite proportions. By the juxtaposition of the different coloured fibres in the yarn, a similar effect is obtained as by dyeing to shade. Thus, almost any shade of grey can be obtained in woollens by mixing in this manner, black and white. In light shades, especially, the colours thus obtained in the finished material are far superior in fastness to light to such as are dyed in the piece. In the manufacture of worsteds, the process of *melanging* has a similar object in view. The slubbing is printed across in stripes, the colours being fixed by steaming; in the subsequent process of drawing, the colours become mixed with the whites in between the stripes, and an apparently uniformly coloured yarn is the result.

Silk is generally dyed in the yarn. Sewing cotton, as well as cotton, wool, and silk yarns for knitting and embroidery purposes are all dyed in the yarn.

**Dyeing of Loose Fibre.**—For the dyeing of loose fibres, no special appliances are absolutely required, the operation frequently being performed in vats or boilers, in which the material is turned by poles or forks. The use of

\*The special methods and machinery used for Turkey-red, Aniline black, and Indigo are described under these headings.

mechanical appliances for this purpose, in which the dye-liquor is caused to circulate through the mass of the fibres, is, however, finding more and more favour, especially among spinners and manufacturers who do their own dyeing. By the use of such appliances the tendency of the fibres to felt is greatly diminished, the dyeing is more even, and there is a saving in labour. When dyeing in open vessels, the material, after having been thoroughly wetted by boiling with water or soda ash and washed, is mordanted and dyed either in wooden vessels provided with a false bottom and heated by steam, or in copper vessels similar to those used in wool dyeing. There is, indeed, a tendency for the cotton to become matted during the process, thus preventing a free circulation of the dye-liquor, in consequence of which an uneven shade may result; but the unevenness is no longer noticeable after

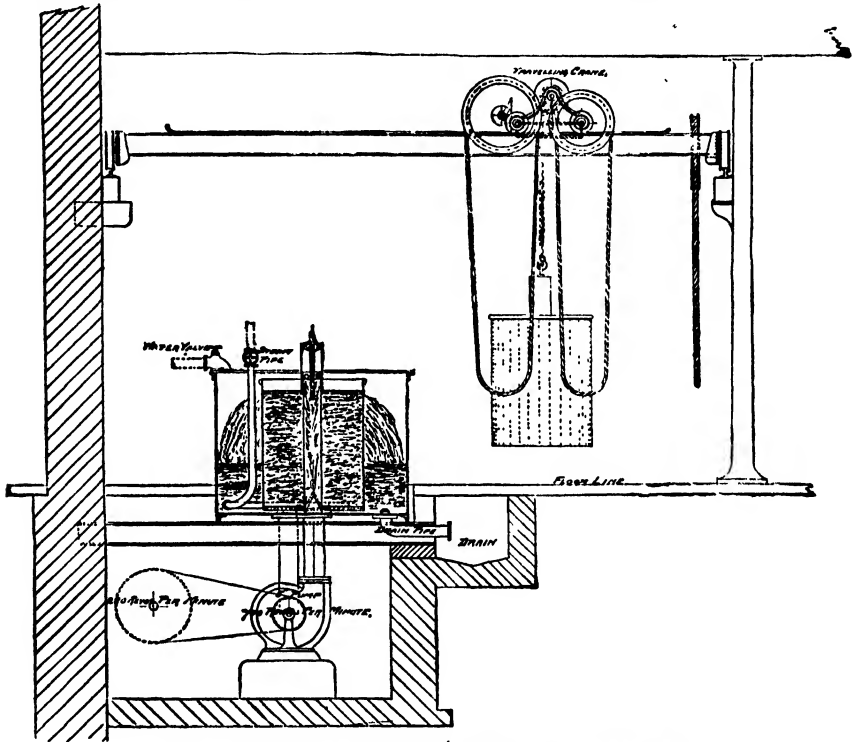


Fig. 68.—Obermaier's dyeing machine for loose fibre.

the carding and spinning, so that, as long as the shade is right in the yarn, this would be no great disadvantage.

The Obermaier apparatus may also be used for the dyeing of loose cotton or wool.

A general view of this apparatus, which was invented by E. Gessler (German Patents Nos. 23,117 and 25,343), will be obtained from Fig. 68, prepared for this volume by the English makers of the machine, Messrs. Mather & Platt. The machine shown in the figure is intended for the dyeing of loose fibre (either wool or cotton), not of tops.

A section of the apparatus is shown in Fig. 69, in which the dimensions are given in millimetres. In this machine the circulation of the dye-liquor is effected by means of a centrifugal pump.

Another machine which may be used for the same purpose, as well as for loose wool and for yarns, is that patented by Schmidt, and shown in plan and elevation in Figs. 70 and 71. In the former the dimensions are given in millimetres.

It consists of two round vats which fit into one another. The outer vat holds the dye-liquor, while in the inner one the material to be dyed is placed.

The inner vat is held by three arms which overhang the edge of the outer vat. It is open at the top, and has in its bottom a number of small openings, which allow the dye-liquor to pass through. The material in this vat, whilst dyeing, is enclosed above and below by copper-wire sieves, in order to prevent it being displaced by the dye-liquor. On the bottom of the outer vat a steam coil is fixed, around which the liquor must pass in rising. By this means the temperature of the dye-liquor and that of the material being dyed is kept almost the same. This is a great advantage which is not met with in other

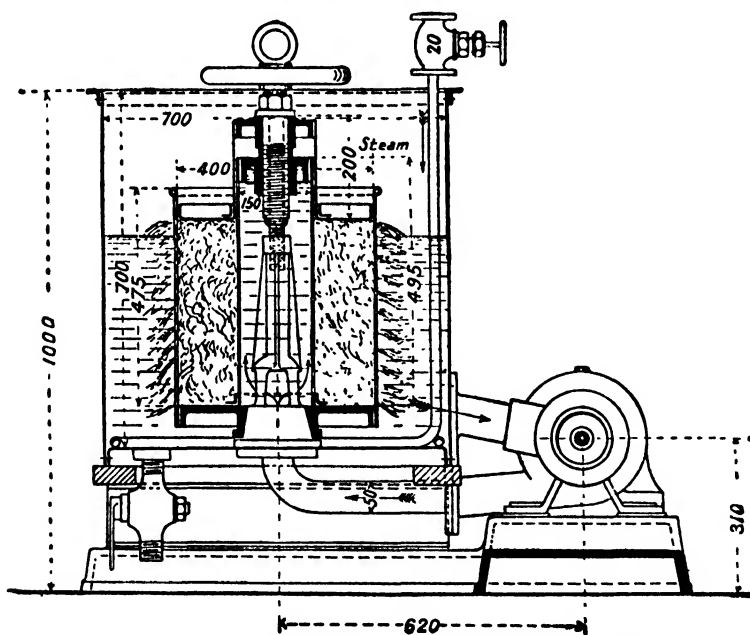
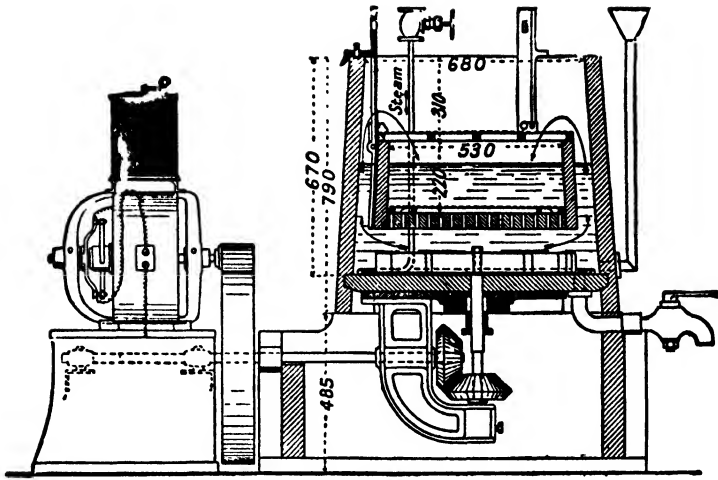


Fig. 69.—Section of Obermaier apparatus for dyeing loose wool.

dyeing systems. Between the bottoms of the two vats a turbine or paddle wheel is placed, which is caused to rotate by bevel wheels driven by an electric motor.

By the rotation of this turbine the dye-liquor between the sides of the vats is forced upwards, and on reaching the top rim of the inner or suspended vat, which is lower than the outer vat, it pours over on to the contents of the former. When the liquid is forced upwards a partial vacuum is formed between the bottoms of the two vats, so that the liquid pouring over the material being dyed forces its way through to the bottom, circulation then commencing again.

In order to add more colour or acid, &c., whilst dyeing, without having to take the material out, as in dyeing in open pans, a pipe is fixed to the side of the outer vat which discharges itself directly on to the arms of the turbine.



Figs. 70 and 71.—Schmidt's dyeing machine (section and plan).

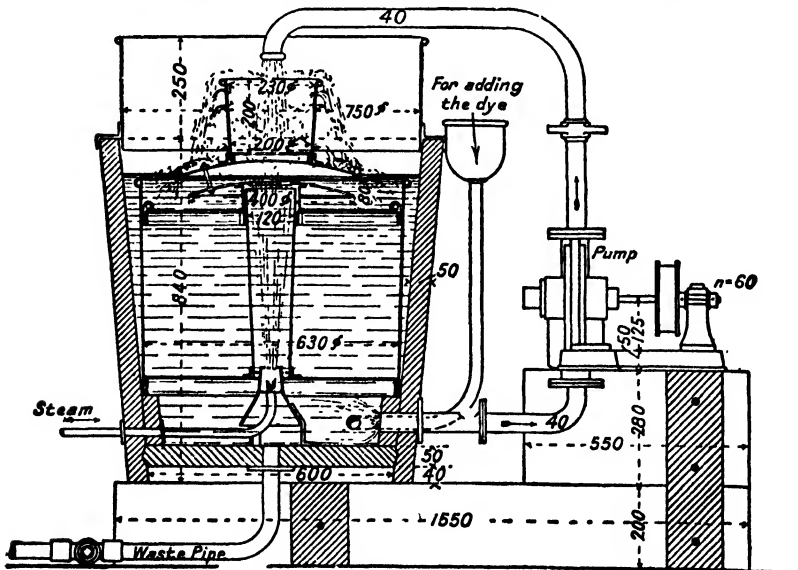


Fig. 72.—Drèze dyeing machine.

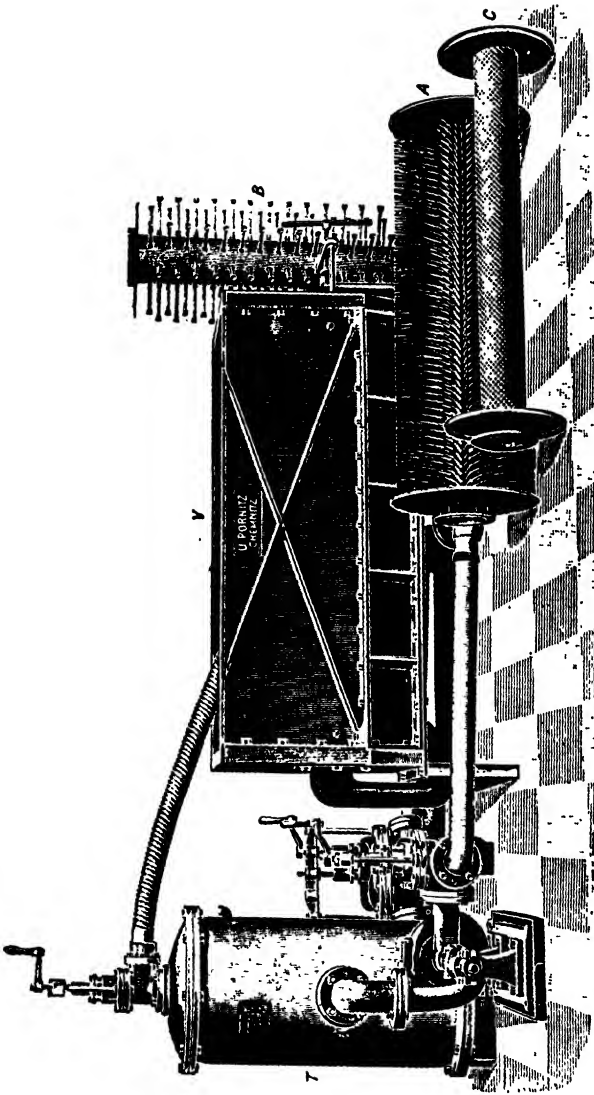


Fig. 73. Open horizontal dyeing or bleaching machine for warper's beams, cops, and cross-wound bobbins.

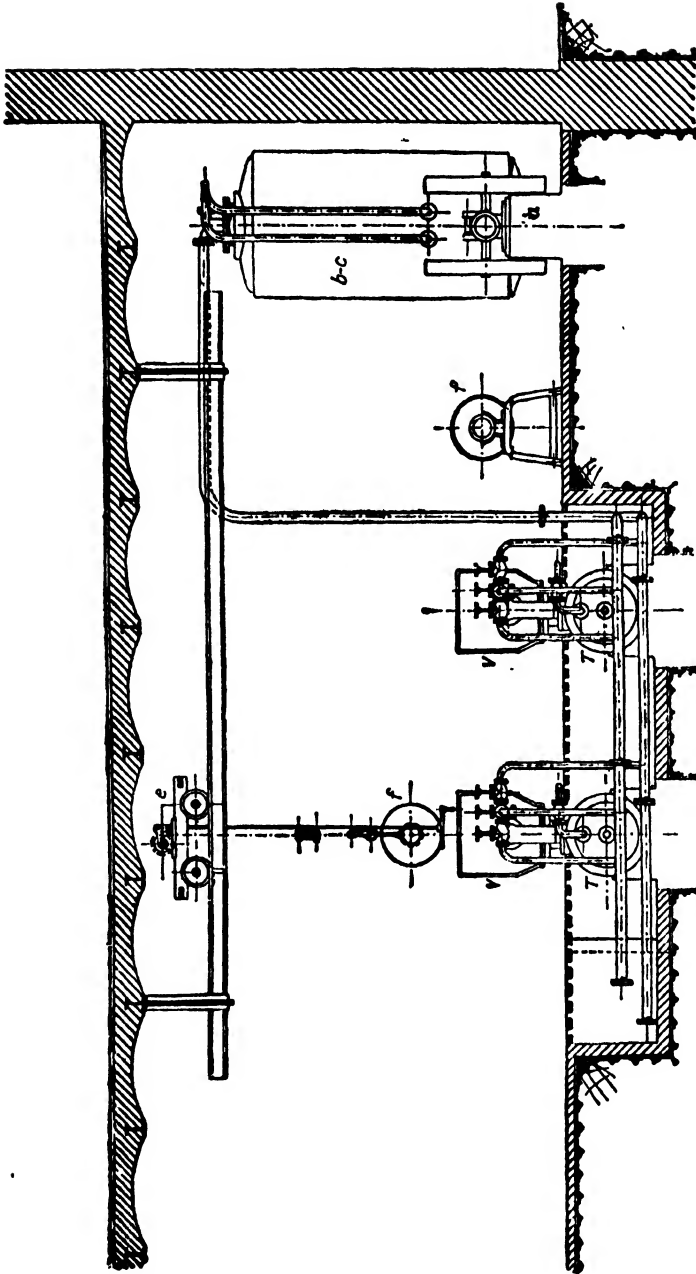


Fig. 74.—Plant for dyeing warps on the beam.

By this means colour, &c., added afterwards is mixed with the whole of the liquor in the shortest possible time, and, therefore, produces no uneven places in the material. The apparatus can be quickly emptied of excess of dye-liquor by the outlet valve in the bottom. The suspended vat is lifted out by a fixed or running crane, according to circumstances.

Dyeing in this apparatus is in general the same as in others, or in open pans. A considerably smaller amount of water is required than with open pans, and, therefore, some precautions are necessary. The copper wire sieves which are covered with well-boiled jute or linen cloth, in order to prevent the so-called copper stains produced by acids, keep the material from moving and becoming matted. Before dyeing, the woollen yarn or other material is well scoured and wetted out, and if possible hydro-extracted, so that it absorbs the dye-liquor evenly.

In laying yarn in the vat care should be taken that the layers are always placed in alternate directions; thus, the hanks of the second layer are placed at right angles to those of the first. This point is of importance, as thereby no open channels are left. The heads of the hanks should not be twisted too tightly, but only sufficiently to enable the yarn, when dyed, to be easily taken out. The hanks should not be tightly pressed, but only laid close together. If these simple directions are followed perfectly even dyeing always results.

The Drèze dyeing machine, which is also intended for loose fibre, is shown in section in Fig. 72. Like the Schmidt machine, it is only suitable for wool; with cotton, the liquor will not pass through. The inner cage, after being evenly packed with the material to be dyed, is let into the outer vat, the circulation and simultaneous heating of the dye-liquor being effected by means of a steam injector which throws the liquor upwards against a metal shield, whence it percolates through the packed cage through the false bottom and is again thrown up by the injector. In case colours are used which are apt to dye unevenly, the dye-liquor is first circulated by means of the centrifugal pump shown in the figure, the steam injector being turned on later.

The same principle is applied by the Zittauer Maschinenfabrik and by Pornitz for the dyeing of warper's beams in a machine like that shown in Fig. 73, which may be used for the dyeing of cops, cross-wound bobbins (cheeses) or beams. Three cylinders are shown in the figure, viz. :—A for cops, B for cross-wound bobbins (cheeses), and C for warps. In the latter case, the cylinder on to which the warps are wound is hollow and perforated. When placed in position in the dye-vat, V, the flanges at each end fit into corresponding flanges in the dye-vat, circulation of the dye-liquor between the cylindrical tank, T, and the dye-vat being effected by means of the centrifugal pump shown in the figure. A somewhat different arrangement is shown in Fig. 74, in which the dye-tank, T, is situated below the dye-vat, V. In this figure, *f* represents the warp beam which is lowered into the dye-vat by means of the travelling crane, *e*; *b-c* represent the vacuum and compressed air cylinders, and *a* the air pump.

*Loose Wool* is usually mordanted and dyed in large hemispherical iron vessels which are heated either by direct fire or steam. Fig. 75 shows a section of a boiler for this purpose, in which the diameters are given in millimetres. In this case the heating is done by indirect steam, the boiler being jacketted. The material is loosely enveloped in the dye-bath with a coarse net, which when withdrawn brings with it the whole of the dyed or mordanted material. During the dyeing, the material is stirred by means of poles or *stangs*.

After mordanting, dyeing, and washing-off, the material is hydro-extracted and dried. In indigo dyeing, the material is wrung after dyeing in the net, so that the liquor can be run straight back into the vat.



**Dyeing of Tops or Slubbing.**—Wool intended for the manufacture of worsteds is not dyed in the raw state, it being preferable to dye it in the form of slubbing (*i.e.*, in the combed state). For this purpose, the tops are unwound and the slubbing is made into hanks, in which form it is dyed. The dyeing of slubbing does not differ essentially from hank dyeing, but the material requires much more care in handling owing to its liability to felt. A certain amount of felting is in many cases unavoidable in the operations of mordanting and dyeing, and this, coupled with the trouble of unwinding the tops and balling them again after dyeing, has called into existence numerous machines in which the tops are dyed as such without having to be unwound. The principle on which these machines are worked is the same as that employed in cop dyeing. The material remains stationary, while the hot mordant- or dye-liquor is either forced or drawn through it.

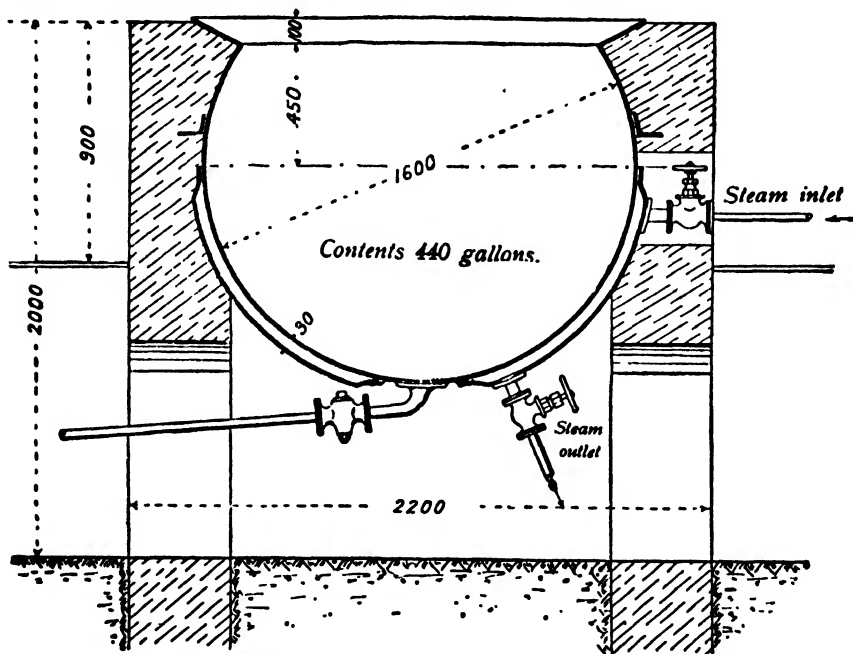


Fig. 75.—Steam-jacketed boiler for dyeing loose wool.

A simple construction of this kind is that patented by Salt & Stead\* and shown in Fig. 76. In the figure three balls of tops,  $x$ ,  $x^1$ , and  $x^2$ , are shown placed in the dye-vat in such a manner that their centers come directly over the pipe,  $b$ , at the bottom. A plate,  $AA$ , is placed on the uppermost ball;  $d$  is a steam pipe for heating the contents of the vat. By means of the centrifugal pump,  $P$ , the dye-liquor is sucked through the material and delivered back into the vat at  $p^2$ .

An apparatus more generally used is that of Obermaier (Fig. 77), the construction of which varies slightly according to the material to be dyed. For tops it consists essentially of a movable copper cylinder,  $B$ , bearing on its circumference 15 to 20 slightly conical receptacles for the tops. The cylinder,  $B$ , stands in the vat,  $A$ , which is heated by steam, and communicates directly with the centrifugal pump,  $C$ .

\*English Patent No. 9690, 1885.

The receptacles of the so-called "revolver cylinder," B, are first filled with tops and closed with perforated copper lids. This takes about 20 minutes for a machine with 20 receptacles capable of holding 160 to 300 lbs. of wool altogether. The cylinder is then placed in position in the dye-vat, to which the necessary additions of dyestuff, &c., have been made. Steam is turned on and the pump is set in motion, which causes the liquor to circulate from the vat through the material and back into the vat again. When the dyeing is finished the whole cylinder is lifted out by means of a crane, the tops are taken out, hydro-extracted, put back into the receptacles, and dried by blowing a current of hot air through the cylinder.

Slubbing is also largely dyed in the Klauder machine (see *Dyeing of Yarn*, p. 708).

Cotton is also sometimes dyed in the sliver in a machine devised by D. Mattei. The sliver is drawn continuously from the tins, is wetted out by

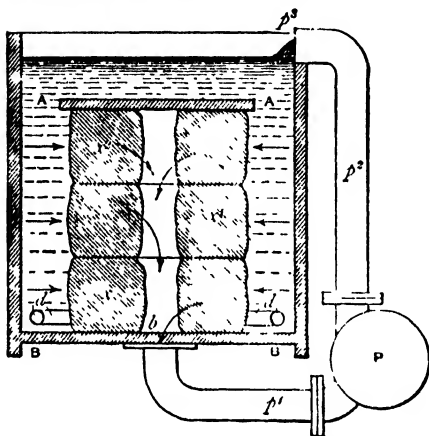


Fig. 76. — Salt & Stead's top dyeing arrangement.

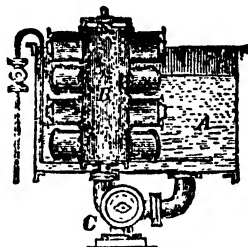


Fig. 77. — Obermaier's dyeing machine for tops.

means of a steam injector, and passes through squeezing rollers into the dye-bath, through which it is guided between two endless perforated india-rubber bands.

**Foam Dyeing.**—This remarkable method of dyeing is especially suited for dyeing cotton in the form of tops, balls, cheeses, &c., and is effected by allowing only the foam of the boiling dye-liquor to permeate the material to be dyed. This is effected in a closed cylindrical vessel, in which the tops, &c., are suspended above the boiling dye-liquor, but do not come into contact with it. The foaming of the liquor is brought about by the addition of soap, Turkey-red oil, saponin, or some similar substance which will cause frothing. By the joint action of the coloured foam and the steam, the material is evenly dyed through.

Foam dyeing is used principally for cotton cheeses, and, to some extent, for cotton cops, but never for wool. The main advantage of the process is the small first cost of the apparatus, and for this reason the method is suitable for small dye-works. The output is, however, small, while the cost of dyeing is somewhat high on account of the large amount of steam required.

**Dyeing of Yarn.**—This is of greater importance than the dyeing of loose fibre, and is applied to all classes of textile materials, such as cotton, linen, worsted, woollen, silk, jute, &c. Yarn is generally dyed in the hank, or in the warp; but cotton yarn is also frequently dyed in the compact form in cops.

*Hank Dyeing.*—Most yarn is dyed in the hank, because this is the most convenient form in which to deal with it. The usual method of dyeing hanks is very simple. For the mordanting and dyeing rectangular vats constructed of wood (pitch pine is the best), stone (generally Yorkshire flag), or metal (iron, or for silk dyeing tinned copper), and heated by steam, are used. Figs.

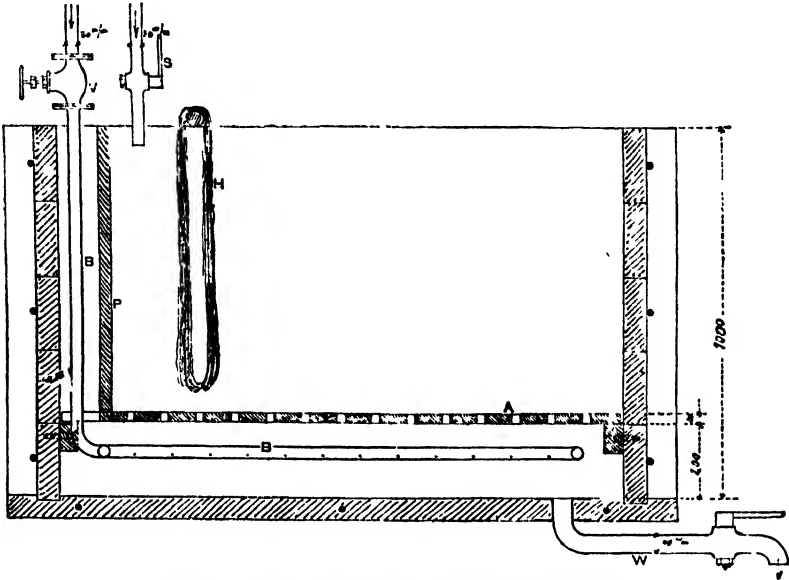


Fig. 78.—Dye-vat for yarn in the hank (section).

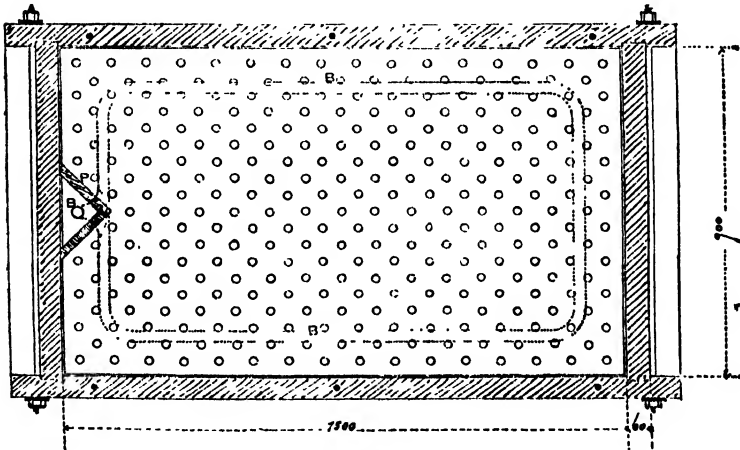


Fig. 79.—Dye-vat for yarn in the hank (plan).

78 and 79 show the construction in section and plan of a wooden vat, such as is ordinarily used in the dyeing of cotton, and of woollen and worsted yarns. It is constructed of strong boards held together by iron bolts, two of which are shown in the plan, while the rest are merely indicated by black dots. A false bottom, A, shown in both figures, serves to protect the yarn from coming

into direct contact with the steam. B is the copper steam-pipe, with steam valve, V, which runs round the vat beneath the false bottom, and is here perforated. In passing down to the bottom of the vat, the steam-pipe is cased off by a wooden partition, P. W is the waste-pipe, and S the water supply. The dimensions given in the figures are in millimetres.

Stone vats are constructed on a similar principle. They are more durable than wooden ones; they are generally met with in old works. Frequently the false bottom is dispensed with, and the steam-pipe, instead of going all round, is simply a straight pipe passing down the middle of the vat, or two pipes passing at each side from one end of the vat to the other. For many purposes iron steam-pipes serve as well as copper ones, and in these cases the cheaper material is, of course, preferred. The friction of the steam in passing through the perforations widens the latter, and when the holes have become too large, the perforated part of the pipe must be repaired or replaced by a fresh one. For working small vats, as is the case, for instance, in silk-yarn dyeing, the heating is advantageously done by means of a movable steam-pipe with a knee-joint. Several vats may thus be heated by means of the same pipe.

In heating by direct steam the liquor in the vat becomes diluted by the water which condenses from the steam. In the majority of cases this does not much matter; but in dyeing certain colours it is necessary to keep the concentration of the dye-liquor constant. To effect this the vat is heated by a steam coil instead of by direct steam. The steam condenses in the coil, and the water formed is drawn off as it forms.

The top of the vat is usually made to stand at a convenient working height (2 feet 3 inches) above the floor level. Consequently large vats, such as are used, for instance, in worsted-yarn dyeing, are let into the ground to a considerable depth.

The following is the *modus operandi* adopted in hank-dyeing. The hanks are suspended in rows on smooth sticks or poles, which are laid across the vat, as shown in Fig. 78, H. The second stick-full comes within an inch or two of the first, and so on, until the vat is filled to within about a foot off the end. The hanks are now turned; a workman stands at each side of the vat; one of them passes a rod immediately beneath the stick holding the last lot of hanks; the other takes it, and the whole stick-full is turned a quarter way round—i.e., so that after two turns the parts of the hanks which were at the bottom are now at the top. The stick-full which was about a foot off the end is now pushed against the end of the vat, and so each set or stick-full of hanks is turned until they come to the other end of the vat. This process is repeated as often as may be necessary during the dyeing or mordanting operation. The number of "turns" during the operation will depend upon the nature of the material and of the dyestuff or mordant employed.

**Hank-dyeing Machines.**—Much hand labour is necessary in hank-dyeing, and this is one of the principal reasons why the process is so expensive as compared with piece dyeing. Many machines have been devised and patented for doing the hand labour required in turning the hanks automatically. In the majority of machines the turning of the hanks in the dye-liquor is effected by substituting for the dye-sticks a series of porcelain rollers which receive an alternate backward and forward motion, all being driven from one shaft by means of spur wheels, as in the hank-washing machine (see p. 726). In other machines of this kind the shaft is dispensed with, and the motion of the rollers is effected from one to the next by toothed wheels. Fig. 80 shows an arrangement of this kind. All the rollers are attached to a frame-work, which, being raised, removes the whole of the material from the dye-liquor, as shown in the machine on the right-hand side. The hanks are weighted at the bottom by metal rods, in order to keep them straight during the dyeing process.

Another common form of hank-dyeing machine consists of two parallel wheels, which turn slowly in the dye-liquor. The hanks are suspended on sticks at the periphery and near the centre, and according to the depth to

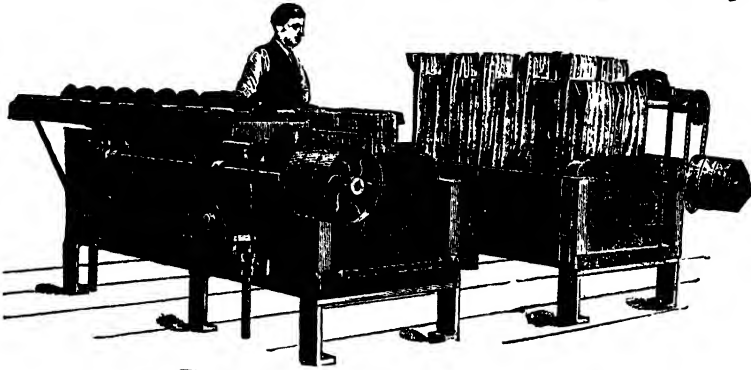


Fig. 80.—Spencer's yarn-dyeing machine.

which the wheels are immersed in the dye-vat they will be exposed more or less to the action of the dye-liquor. Fig. 81 shows an arrangement of

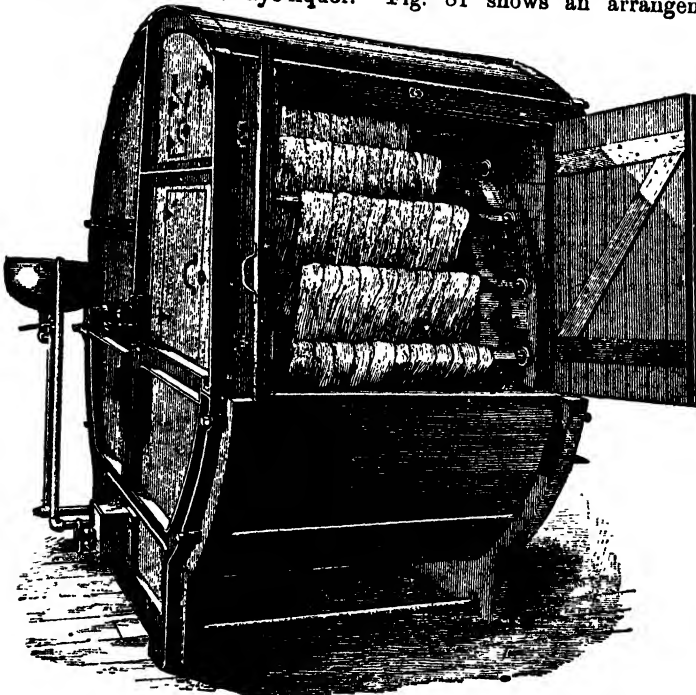


Fig. 81.—Klauder's yarn-dyeing machine.

this kind patented by Messrs. Klauder & Bros. Here the whole wheel is encased in a wooden case, so that while the dyeing is proceeding very little steam gets into the room; the material remains hot when not in the dye-liquor

and there is a saving in steam. By a mechanical arrangement the dye-sticks are also caused to revolve slowly while the machine is in operation.

Another device for causing the dye-sticks to revolve in a system of this kind is due to Messrs. Sykes & Heppenstall of Huddersfield. Loaded discs are placed at the ends of the dye-sticks, which cause them to revolve slowly as the wheel turns in the dye-vat.

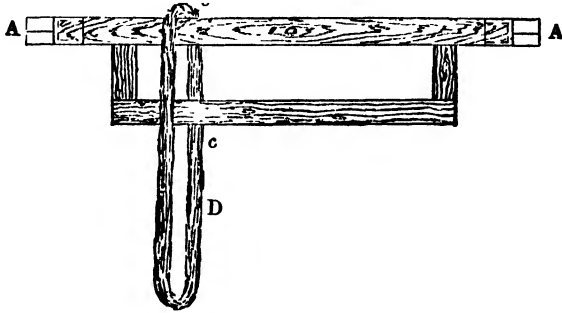


Fig. 82. —Dye-stick for Corron's yarn-dyeing machine.

Another principle is adopted in the yarn-dyeing machine of C. Corron, which is constructed on a principle, the object of which is to imitate as nearly as possible the usual hand labour. The dye-sticks, which rest loosely in slots in the sides of the dye-vat, have a framework attached to them (see Fig. 82). By means of an ingenious, but complicated, mechanical device they are automatically lifted, one after the other, turned, and placed back in the dye-bath, not in the same place, but a few slots further back. By turning the stick right round on its axis,  $\Delta \Delta$ , the hanks will be turned by double the distance,  $c, c$ , and the point marked  $D$  will then be uppermost.

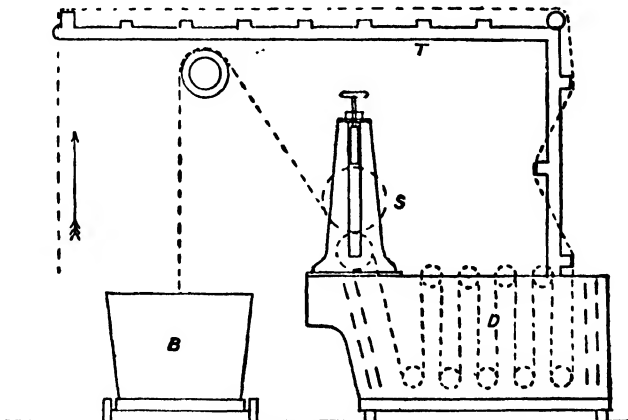


Fig. 83. —Single-box warp-dyeing machine.

**Warp-Dyeing.**—Warps are sometimes dyed in the hank form, but for large quantities, especially of cotton warps, warp-dyeing machines are more advantageous, the dyeing being done much more rapidly and with much less labour than in the hank.

Fig. 83 shows a section of a single-box warp-dyeing machine, in which the warps are shown travelling in the direction of the arrow, over the trellis,  $T$ ,

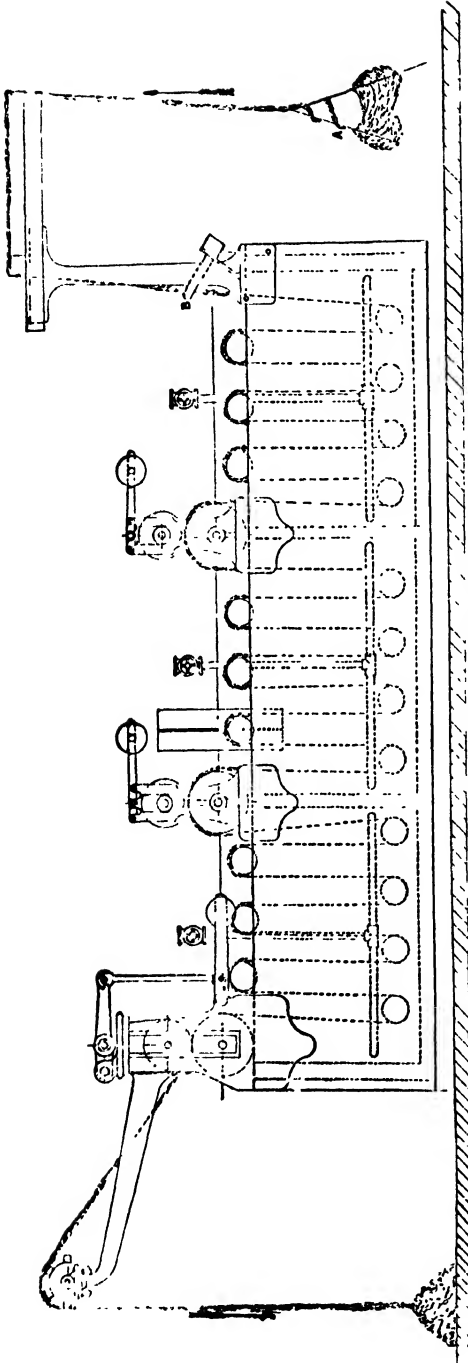


Fig. 84.—Warp-dyeing machine with three compartments (Mather & Platt).

through the steam-heated dye-bath, D, thence through squeezers, S, and into the bin, B.

Fig. 84 shows a warp-dyeing machine with three compartments. It consists of a wooden vat divided into three compartments, each of which can be heated by steam. Between each compartment and at the end of the third, squeezing rollers are placed, and each compartment is fitted with three copper rollers above and four below. The three compartments may serve to contain three different liquids or they may all contain the same, as may be required.

In the working of the machine, the warps are drawn from the balls, A, pass over two rails above, and through the guides, B (which serve to keep them separate), into the first compartment. Here they pass up and down through the liquid and out through the squeezing rollers into the second trough, and so on until they leave the machine through the last pair of squeezing rollers at the end of the third compartment. If the desired shade has been obtained after passing once through the machine, they are said to have been dyed in "one end." Generally, one passage through the machine is not sufficient, and in such cases the warps pass back over lattice-work at the top of the machine into the first compartment again and go through the operation, or series of operations, a second or third time or until the shade is obtained.

Warp-dyeing machines are also constructed with less than three and with more than three compartments according to the special purposes for which they are to be used (see Fig. 83). The dye- or mordant-liquor or the water used for washing-off

is made to pass through the compartments in a direction opposite to that followed by the warps.

For indigo dyeing, a special form of machine is frequently used, like that shown in section in Fig. 85, which was devised by W. H. Pennington, and is constructed by J. Jackson, Todmorden.

It consists essentially of a strong framework, F, carried on four wheels. The inner framework carrying the guiding rollers can be raised or lowered by means of the chain, C, and is kept in position by means of rods, R, which slide through holes in the lower part of the frame. The squeezer, S, is attached to the frame. In the figure, the framework carrying the guiding rollers is shown lowered into the vat, V. When the dyeing in this vat is finished, the framework is drawn up into the main frame, which is then wheeled on to the next vat, where dyeing with a stronger or weaker vat proceeds again as in the first case.

Warps are now also largely dyed on the "beam" in machines like that

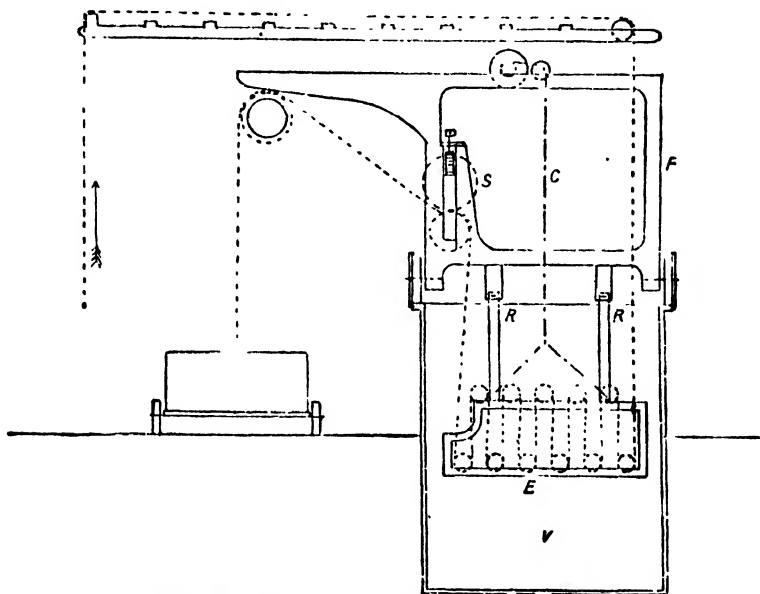


Fig. 85.—Warp-dyeing machine for indigo vats.

shown in Fig. 73, in which the dye-liquor is aspirated or forced through the perforated cylinder on which the warp is beamed.

**Cop-Dyeing Machinery.**—As the cotton yarn is formed on the spinning frames, it is wound automatically into so-called "cops." In order to save the time and labour necessary for reeling these cops into hanks for the purpose of bleaching and dyeing and rewinding into the cops so as to fit into the shuttle various devices have been suggested, and numbers of patents have been taken out for machines the object of which is to dye the yarn in the cop without having to unreel it. Besides effecting a saving in time and labour, the method reduces to a minimum the danger of damaging the yarn. In nearly all these patents one and the same principle is adopted—viz., the dye-liquor is either forced or sucked transversally through the mass of the cop. After the grease and wax have been got rid of by boiling the cops in alkali (see p. 93), this would not appear to present any great difficulty. In



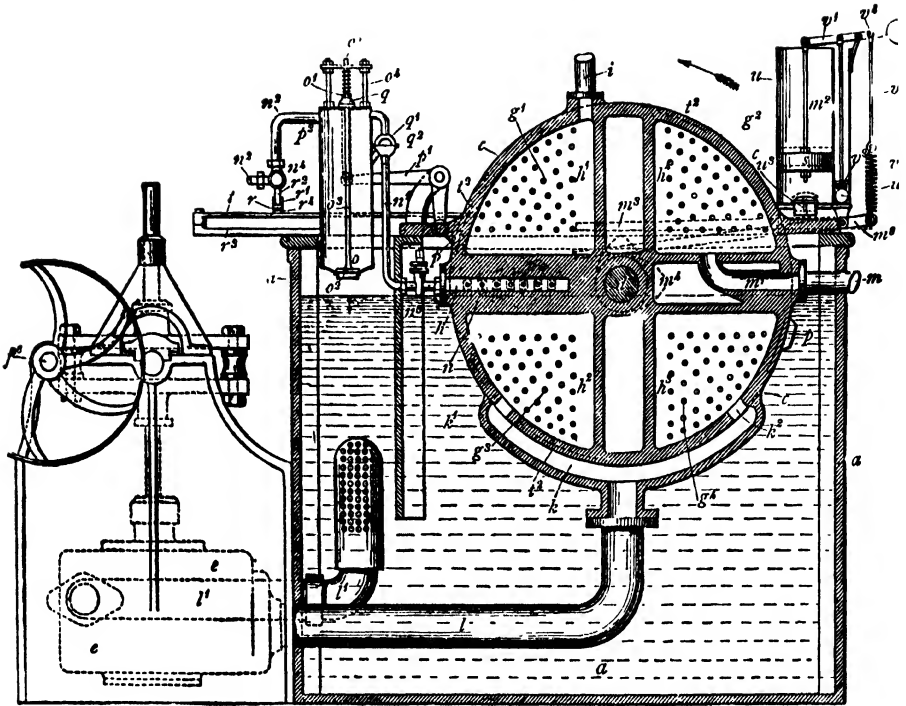


Fig. 86.—Graemiger's cop-dyeing machine (section).

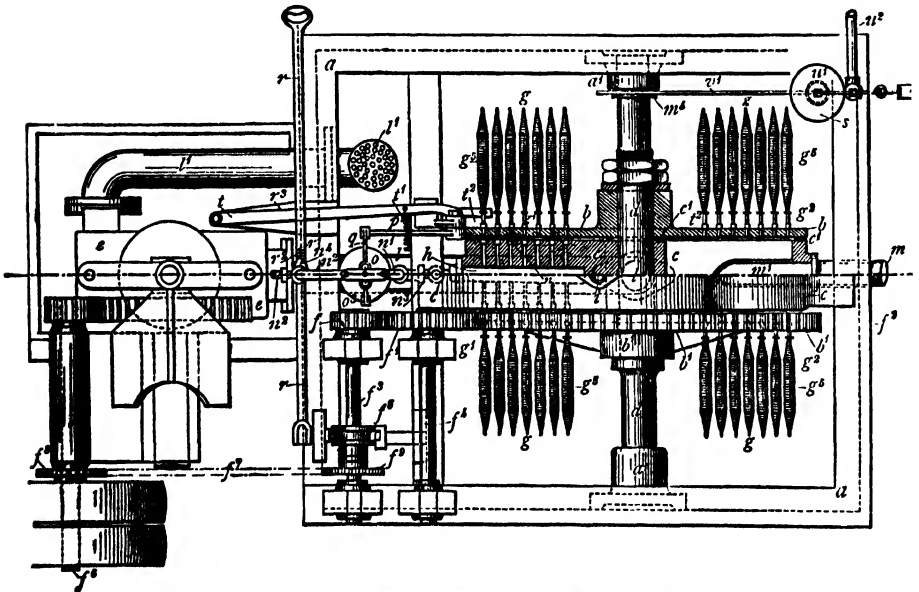


Fig. 87.—Graemiger's cop-dyeing machine (plan)

practice, however, great difficulties have been experienced, more especially in the production of even shades or colours. Nevertheless, cop-dyeing has, during the last twenty years, made steady progress, and there are at present many establishments in which large quantities of cotton are dyed in the cop. A great impetus was given to this kind of dyeing by the introduction of the direct cotton colours, most of which possess in an eminent degree the property of penetrating and dyeing level. It is obvious that only such dyes as are completely soluble in water can be used for the purpose, for if it were attempted to force such a colouring matter as Alizarin through the cop, the mass of cotton would simply act as a filtering medium, and, as a consequence, only a very small proportion of the yarn would be dyed, the rest remaining white or at most tinged.

The dyeing of yarn in the cop is effected in two different ways. According to the first of these, each cop is stuck on to a hollow perforated tapering spindle or skewer, the lower extremity of which is in turn inserted in a perforated plate or cylinder. When all the apertures in the plate or cylinder are filled, the dye-liquor is forced through the cop by suction or pressure. According to the other system, solid wooden skewers are first inserted in the cops to prevent their collapsing, and the latter are then packed as closely

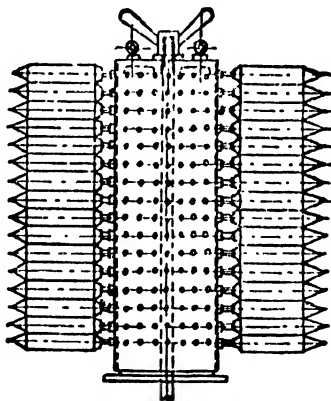


Fig. 83.—Section of cylinder with cops attached in Pornitz's cop-dyeing machine.

together as possible in a box, the intervening spaces being filled with cotton waste, sand, or ground cork. The dye-liquor is then circulated through the box by a suitable contrivance.

One of the first of these cop-dyeing machines introduced was that devised by Graemiger,\* and subsequently improved upon by Graemiger, Whitehead, Mason, and Leigh.† Figs. 86 and 87 show section and plan of this machine.

The machine (Figs. 86 and 87) has four chambers,  $h^1$ ,  $h^2$ ,  $h^3$ , and  $h^4$ , shown in the section. The two lower chambers are immersed in the liquor of the dye-vat,  $a$ , and are connected with a pump which causes the dye-liquor to circulate, being drawn off through the pipe,  $l$ , and re-entering the vat by the pipe,  $l^1$ . Of the two upper chambers,  $h^1$  is connected with an air pump, and  $h^4$  with a liquor pump. The cops are stuck on the cop-carrier discs,  $b$ ,  $b^1$  (plan), which fit hermetically against the walls of the chambers. The discs are fixed on the axis,  $d$ , and are intermittently rotated by means of spur wheels,  $f$ ,  $f^1$ ,  $f^2$ , shafts,  $f^3$  and  $f^4$ , and clutch,  $f^5$ , from the driving shaft,  $f^6$ , through the chain,  $f^7$ , and wheels,  $f^8$  and  $f^9$ .

\* English Patent No. 11,497, 1887.

† English Patent No. 9,692, 1889.

The *modus operandi* is as follows:—Those portions of each cop-carrier disc corresponding to the chamber  $h^1$  having been filled with cops, the discs are caused to make a quarter revolution. The cops thus come opposite chamber  $h^2$ , which being in connection with the suction pump, sucks the dye-liquor through the mass of the cops. With the second quarter-revolution

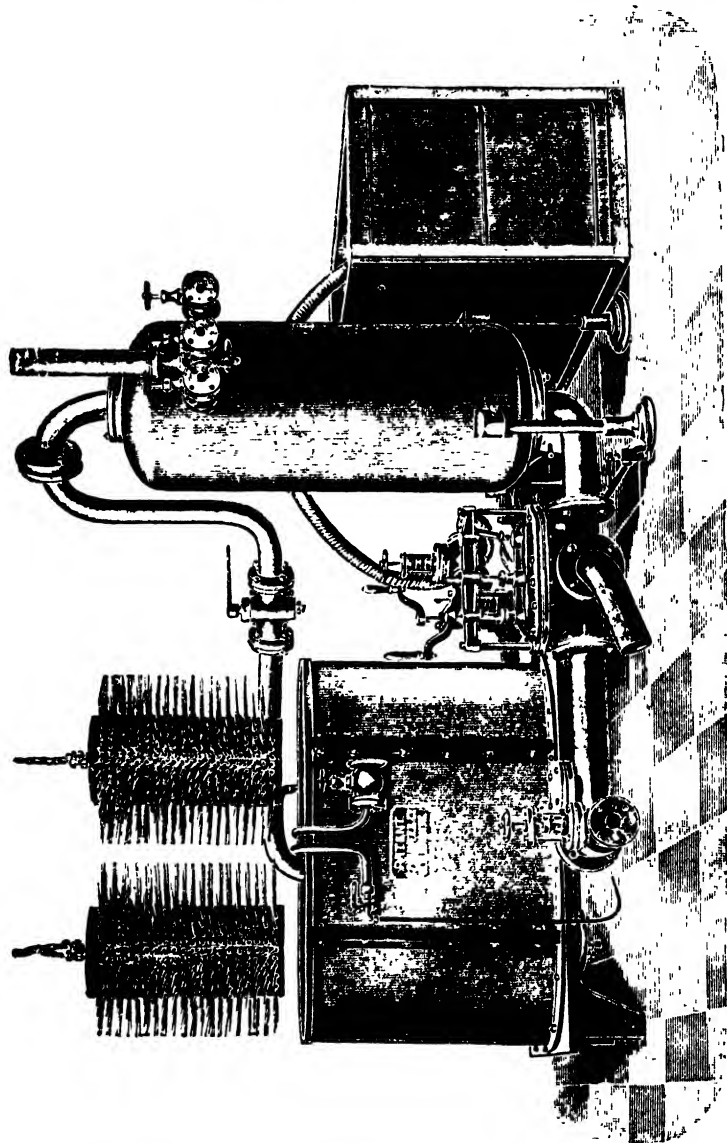


Fig. 89.—Open cop-dyeing machine (Forntz).

the cops come opposite chamber  $h^3$ , when practically the same takes place as in chamber  $h^2$ . With the third quarter-revolution the cops are brought opposite chamber  $h^4$  where the superfluous dye-liquor is drawn off through the pipe  $m^1, m$ . With the fourth quarter-revolution, lastly, the discs are brought back again to their original position. They are removed and replaced

by fresh ones. The dyed cops are dried in another apparatus by sucking hot air through them.

Another form of cop-dyeing machine, the action of which is based upon the same principle as that of Graemiger, is constructed by The Zittauer Maschinen-Fabrik and by Messrs. U. Pornitz & Company. In this machine the skewered cops, instead of being attached to a perforated plate, as is the case in the former, are attached to a hollow, metal cylinder closed at the top, shown in section in Fig. 88. Each cylinder thus charged is capable of carrying from 55 to 80 lbs. of cotton yarn. Two such cylinders are then inserted in an open dye-vat, as shown in Fig. 89, and by means of hand screws are connected with the pipes at the bottom of the vat leading to the centrifugal pump, which

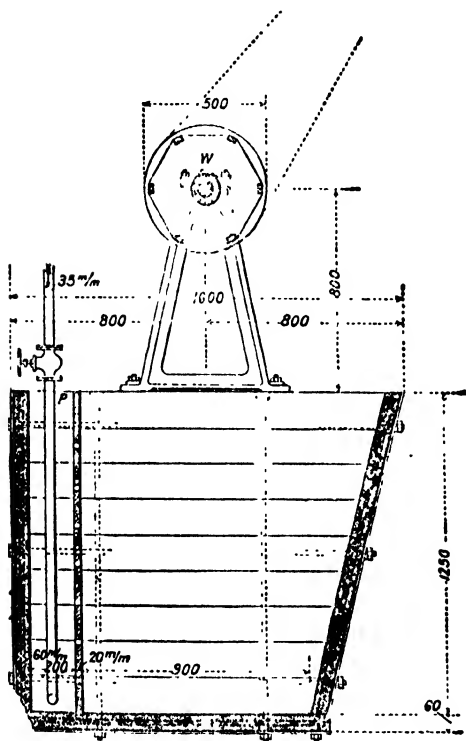


Fig. 90. — Dye-vat and winch for piece-goods (cross-section).

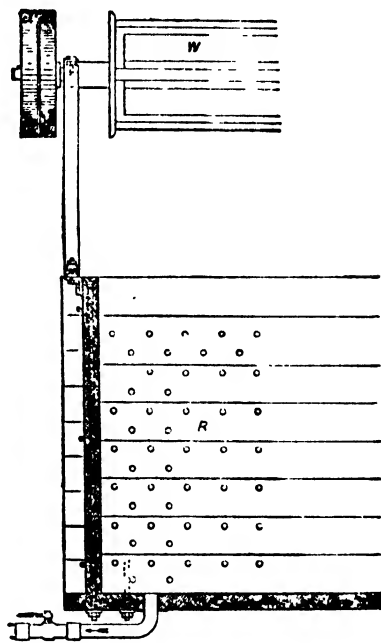


Fig. 91. — Dye-vat and winch for piece-goods (vertical section).

effects the circulation of the dye-liquor from the closed upright cylinder on the right. When the dyeing is finished, the dye-liquor is drawn off by the pump into the rectangular vat shown in the figure for further use.

Numerous other forms of cop-dyeing machines, which work on the perforated skewer system, have been patented, but those which are of any practical value differ but slightly in principle from the two described above. In dyeing by the compact (solid skewer) system, a machine like that of Obermaier (Fig. 68) can be used. A square vessel is, however, more suitable for packing the cops than a round one.\*

\* For a fuller account of these machines see articles by P. Maguire, *Journ. Soc. Dyers and Col.*, 1906; also Ullmann's book, *Die Apparatefärberei*.

In cop-dyeing, the principal difficulty encountered is to dye the cops evenly throughout. In order to attain this end various precautions are necessary,

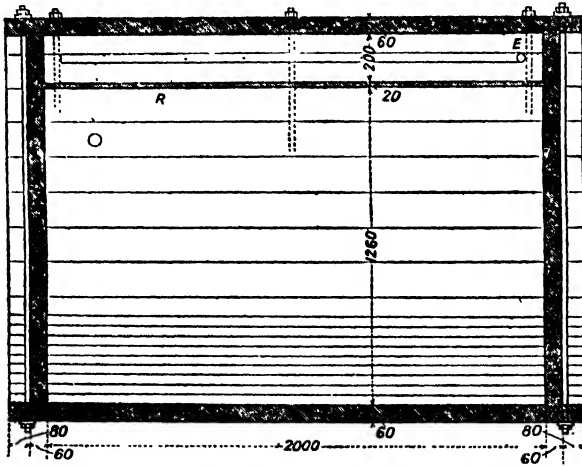


Fig. 92.—Dye-vat and winch for piece-goods (plan).

such as regular winding, the choice of the right kind of paper for the spools (it should not contain any soluble alumina salts), suitable and properly perforated spindles (skewers), good circulation of the dye-liquor, &c.

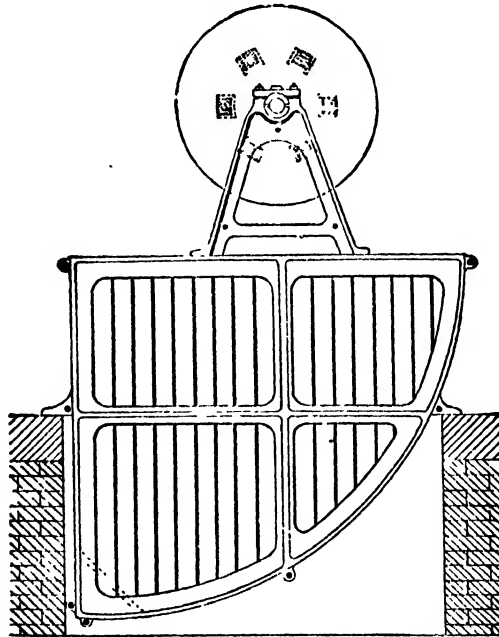


Fig. 93.—Dye-vat and winch.

Latterly, wool cops have been successfully dyed in machines like those of Wolff (Schweinsburg) and of Colell & Beutner (Crimmitschau), in both of

which the course of the dye-liquor is automatically reversed every two minutes.

**Piece Dyeing.**—In cotton, woollen, and worsted goods and in mixed fabrics, dyeing in the piece by far exceeds in importance the dyeing of these materials in any other form.

Piece goods are almost invariably dyed by machinery, except in job-dyeing, where much hand labour is still used.

The simplest form of machine for dyeing pieces is the dye-vat and winch. The construction of a machine of this kind is shown in cross-section, vertical

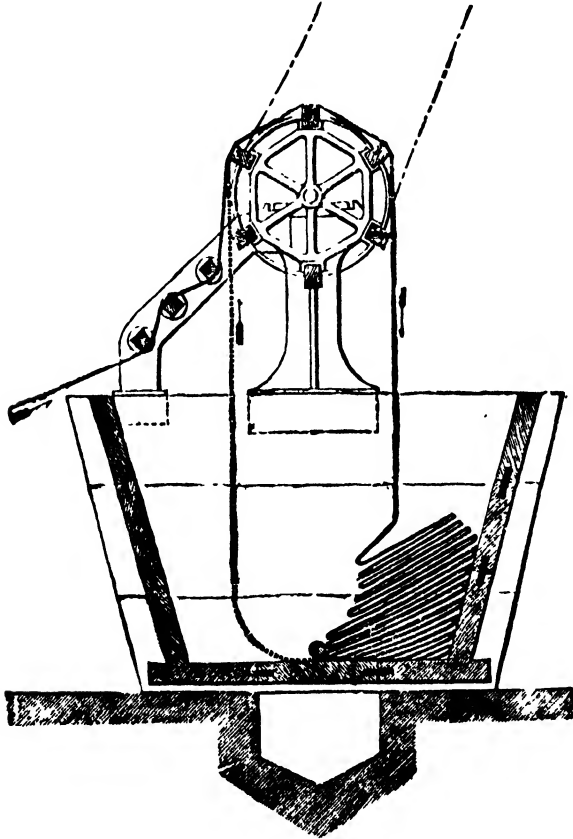


Fig. 94.—Jig winch.

section, and plan in Figs. 90, 91, and 92, in which the measurements are given in millimetres, and are calculated for a machine capable of dyeing about 220 lbs. of woollen cloth. The vat is constructed of wooden boards held together by iron bolts, some of which are shown, while others are merely indicated by black dots. The heating is done by direct steam by means of the copper pipe, P, which enters at one end (at E) and runs along the whole length of the vat. A perforated wooden partition, R, serves to keep the pieces from coming into direct contact with the steam-pipe.

By means of the winch, W, the pieces stitched together so as to form an endless band are caused to circulate continuously through the dye-liquor during

the operation of mordanting or dyeing. Frequently the pieces are arranged on the same winch in the form of several endless bands, parallel to each other and separated by lattice work, so as not to become entangled. Here the winch is shown to be driven by belt and pulley, but in some works this is still done by hand by means of a handle. In a machine of this kind, all the operations of scouring, mordanting, dyeing, and washing-off may be effected.

Another form of dye-vat largely used in woollen and worsted piece dyeing is that shown in Fig. 93. The bottom is curved in place of being flat as in the previous construction.

Fig. 94 shows another similar arrangement by Messrs. Mather & Platt more adapted for dyeing heavy cotton goods in colours, and known as a *jig winch*. The same machine may also be used for washing-off after dyeing in jiggers, and for dyeing small lots of warps. To the same firm, the authors are indebted for an engraving (Fig. 95) of their copper-cased dye-beck, in which the heating of

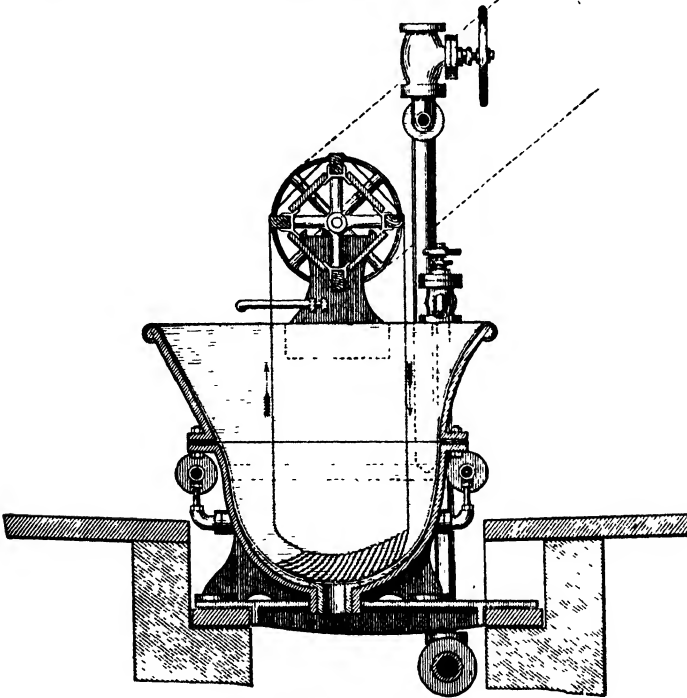


Fig 95.—Copper cased dye-beck (Mather & Platt).

the liquor is effected by the admission of steam into the hollow space at the bottom of the vat, a dilution of the dye-liquor during the dyeing operation thus being avoided. This is important in certain special cases, such as the dyeing of aniline black or of the direct cotton colours.

Another form of machine largely used for cotton pieces, especially in Alizarin dyeing, is shown in vertical section, side view, and cross-section in Figs. 96 and 97. This dye-vat is constructed of cast iron.

The pieces stitched together end to end enter at the left-hand end of the machine (Fig. 96), pass over the winch down into the dye-liquor, in which they are caused to remain for a short time by allowing them a certain amount of slack. Thence they are drawn out again, passing between the first and second

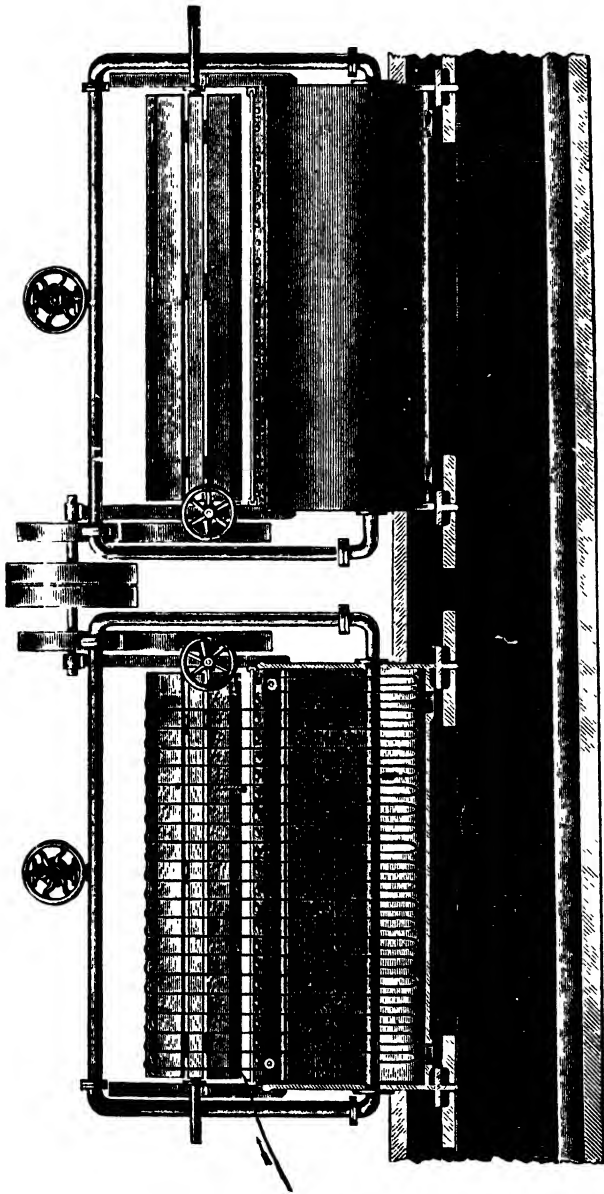


Fig. 96. — Dye-beck for cotton pieces (Mathor & Platt).



guide pegs, over the winch again, and so on, thus traversing the whole machine in a spiral form. When the first piece has arrived at the end of the winch, it

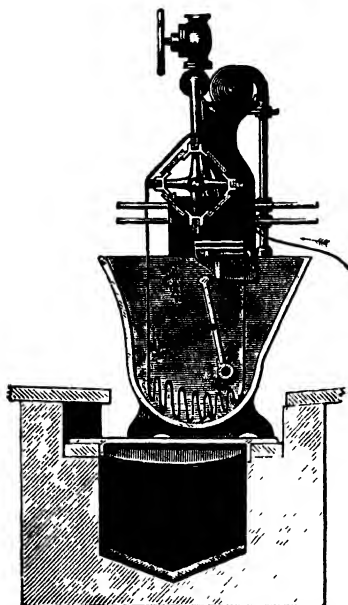


Fig. 97.—Cross-section of Fig. 96.

is passed back again over a small roller shown in the figure, and over another roller at the other end to where it entered, and is there stitched to the end of

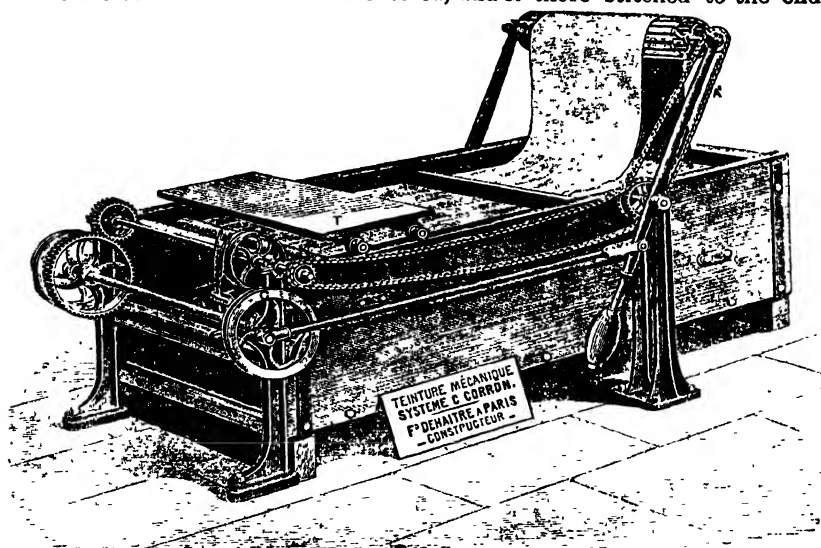


Fig. 98.—Corron's piece-dyeing machine.

the last piece, thus forming an endless band. A machine of ordinary dimensions is capable of taking 20 to 30 pieces at a time.

A machine which imparts to the pieces a double movement in the dye-bath, and which is said to be specially suitable for the dyeing of pile-fabrics, is that devised by C. Corron, and shown in Fig. 98. The driving gear not only causes the winch to revolve by means of the chains, A and A', but imparts to it simultaneously by the crank-wheel, C, and the connecting-rod, B, a to-and-fro

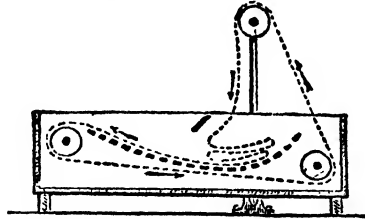


Fig. 99.—Section of Corron's piece-dyeing machine.

motion. The manner in which the pieces pass through the dye-vat is clearly indicated by the sectional sketch in Fig. 99.

The machine which is most extensively used in the dyeing of cotton piece goods (also sometimes in bleaching and in dyeing the cotton in mixed fabrics) is the so-called *jigger*, shown in Figs. 100 and 101.

Fig. 100 shows a view of two dyeing jiggers, in one of which part of the side is broken away to show the manner in which the pieces pass through.

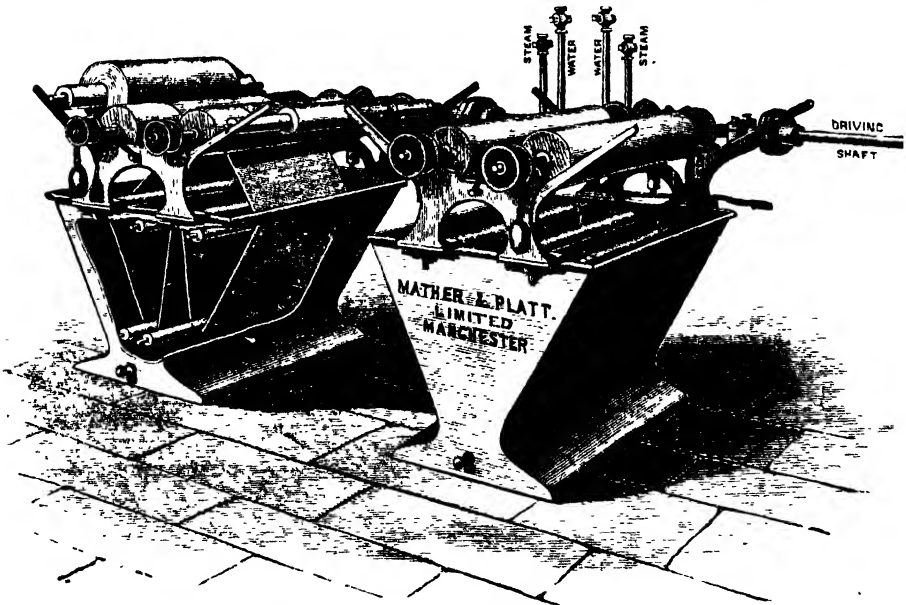


Fig. 100.—Dyeing jiggers (Mather & Platt).

This is also shown in the section. The modern jigger consists of a wooden or cast-iron dye-vessel heated by steam and provided with water supply and waste-pipe. In the vessel are three rollers, R (Fig. 101), at the top and two, R', at the bottom, which guide the pieces in their passage through the dye-liquor. In the section they are being drawn from roller B on to roller A, passing twice

down and up through the dye-liquor before reaching A. During this passage the roller A is driven by a bevelled wheel from the driving shaft (Fig. 101), the pieces being kept in a state of tension by means of a brake (shown in Fig. 100) on roller B. When roller B is empty the order is reversed; B is then connected with the driving shaft, and the brake is put on A. This alternating action goes on until the pieces are dyed, when they are run straight off on to the "batch roller," W, which may be placed on either side of the jigger as desired.

For colour dyeing, the jigger is a most convenient form of machine. The pieces pass through at their full width, and do not remain for a long time in the dye-liquor. As the dyer can conveniently approach the machine from any side, he can at once see how the operation is going on.

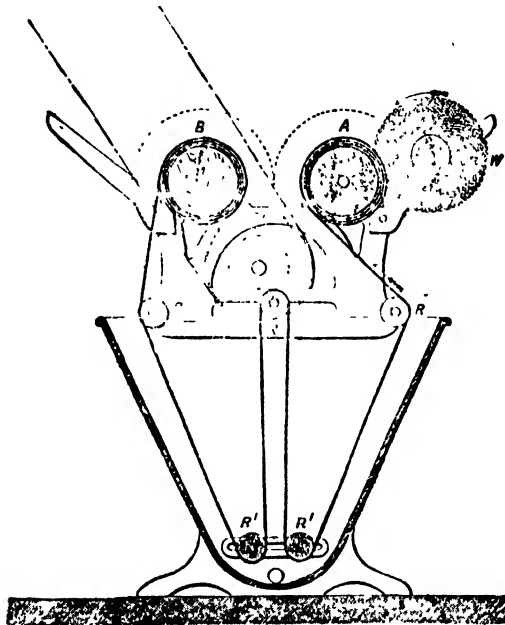


Fig. 101.—Dyeing jigger (section)—Mather & Platt.

After the pieces have been "batched," it is not advisable to allow them to lie in one position for any length of time, as the dye-liquor which they retain mechanically would sink by gravitation to the bottom, and the lower layers would be liable to become dyed a darker shade than the upper ones, thus giving rise to unevenness. It is best to wash off as soon as possible after dyeing.

For dyeing sulphide colours, jiggers provided with squeezing rollers are largely used. For this class of colours and for vat dyes of the Indanthrene series, a form of jigger is also in use in which the batch rollers are submerged in the dye-liquor.

**Padding Machines.**—The use of padding machines is almost entirely restricted to the treatment of cotton piece goods, either for dyeing them in the concentrated solution of some direct cotton colour or sulphide colour, or for preparing with various mordants which are afterwards fixed by ageing or otherwise, also for preparing with beta-naphthol. In principle, the construction of an ordinary padding machine is very simple. It consists essentially of a vessel

(Fig. 102) of comparatively small size, holding the colour or mordant solution, and a pair of squeezing rollers. The pieces are drawn from the batch roller through the liquid in the vessel or trough and thence through the squeezing rollers superposed. The excess of liquid is thus uniformly expressed, and the

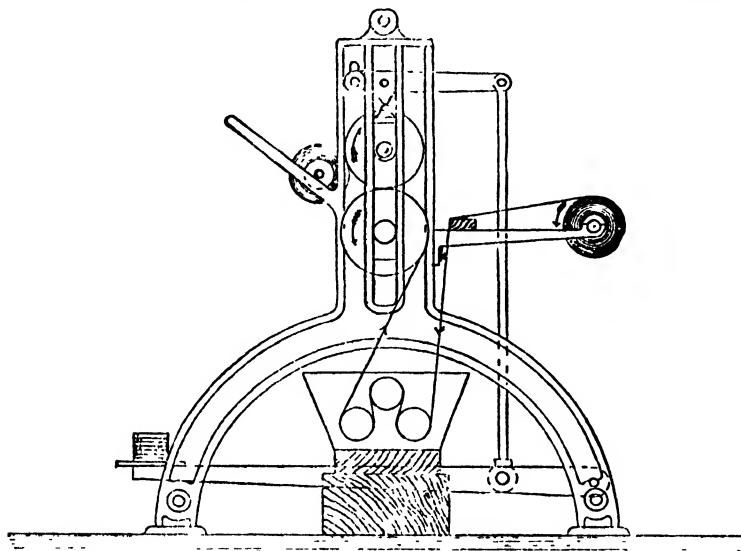


Fig. 102.—Padding machine.

pieces are either batched again on the other side or pass away directly to another operation.

Padding machines may also be employed for dyeing in place of jiggers, by increasing the size of the vessel A, and providing a larger number of rollers by which the pieces are caused to pass several times up and down through the

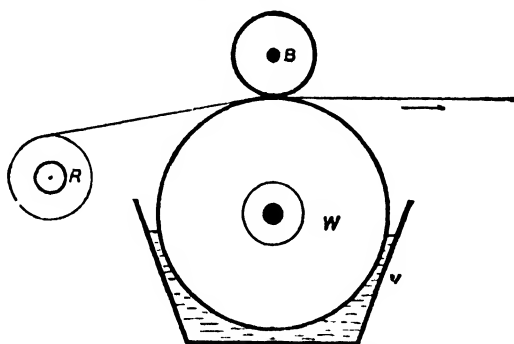


Fig. 103.—Sloop-padding machine.

liquor. When batched after having passed through the squeezers, there is less danger of the pieces becoming uneven through after-dyeing.

The simplest form of padding machine is the sloop-padding machine, the principle of which is shown in Fig. 103. The pieces are drawn from the batch roller, R, between two bowls, B and W, made respectively of brass and sycamore. The bowl, W, runs in the padding liquor contained in the trough,

V. At the point of contact of the two bowls the pieces are simultaneously impregnated with the liquor and squeezed, thus becoming thoroughly impregnated. This machine is especially adapted for preparing cotton piece goods with Turkey-red oil, tannic acid, and beta-naphthol.

For padding on one side only a single-colour printing machine is frequently employed.

The piece passes round the large iron roller, A (the bowl), which presses against the engraved copper or brass printing roller, B (Fig. 104). The latter presses against the furnishing roller which runs in the thickened colour or mordant contained in the colour box, C. The whole surface of the printing roller is engraved diagonally with fine diagonal lines in such a manner as to enable it to take up more or less of the colour (according to the depth of the engraving). By means of a smooth steel blade or "doctor," D, the excess of colour is scraped off the printing roller, which retains, after having passed it,

only what colour remains in the engraving. This becomes transferred to the piece at the contact of B and A, impregnating the latter with the colour in a uniform manner. Between the piece and the bowl there passes an endless band of thick felt, E (the blanket), the object of which is to provide an elastic layer between the bowl and printing roller. Between the blanket and the cloth to be printed a "back-cloth" is usually run in order to prevent the blanket from becoming soiled.

Dissolving of colours.—All soluble dye-stuffs should be carefully dissolved in condensed water before adding to the bath, and although not in all cases necessary, it is at least advisable to sieve or filter the solutions through muslin or thin calico. The necessity of this precaution will be evident when it is borne in mind that some of the coal-tar colours are apt to contain small quantities of highly coloured resinous or tarry impurities insoluble in water. If these get into the goods the latter are spoiled, and a remedy is in many cases impossible. Pastes and

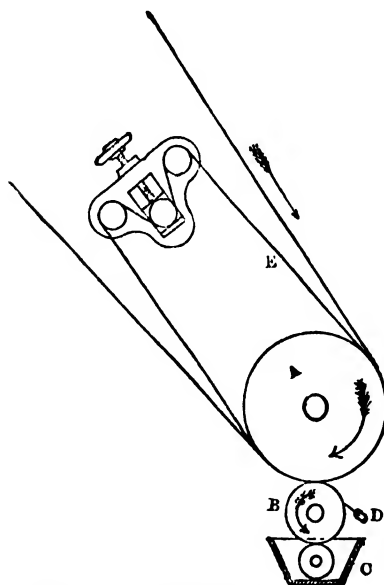


Fig. 104.—Single-colour printing.

extracts are stirred with water to a uniform thin consistency, and should be sieved before being added to the bath. In many large works the mordants and the principal dyestuffs in use (*e.g.*, blacks, logwood extract, &c.) are kept in solution in storage tanks. The strengths of these solutions being known, the amounts required are simply measured, and the dyer is saved the time and trouble involved in weighing and dissolving.

Soluble coal-tar colours, extracts, and paste colours may be added to the dye-bath at once, or, if they are apt to "flush"—*i.e.*, to go on too rapidly and thus cause unevenness—they may be added by degrees. In the dyeing of wool, dyewood extracts (especially logwood extracts) are not largely employed, practical experience having shown that better colours are obtained by using the chipped or ground dyewoods; this method is at the same time decidedly more economical. It is not advisable to add the chipped or ground wood to the dye-bath in the loose form, as it would adhere mechanically to the material, and some trouble would afterwards have to be taken to get it out again. A

common method of overcoming this difficulty is to put the amount of dyewood or dyewoods necessary for the desired shades into bags, and allow them to boil for 20 minutes or so in the vat before entering the goods. Once boiling is, however, not sufficient to extract the colouring matter, and, in order to avoid a loss in this manner, it is usual in many works (especially in black dyeing) to boil the bags three times—*i.e.*, in preparing the bath one bag is used containing fresh colouring matter, one which was imperfectly extracted in the operation before, and the third from the last operation but one (see p. 332).

An ingenious device for completely extracting the dyewood, and at the same time heating the dye-vat and causing a circulation in it, is due to Mr. S. Smithson. The apparatus (shown in Fig. 105) consists essentially of a pair of

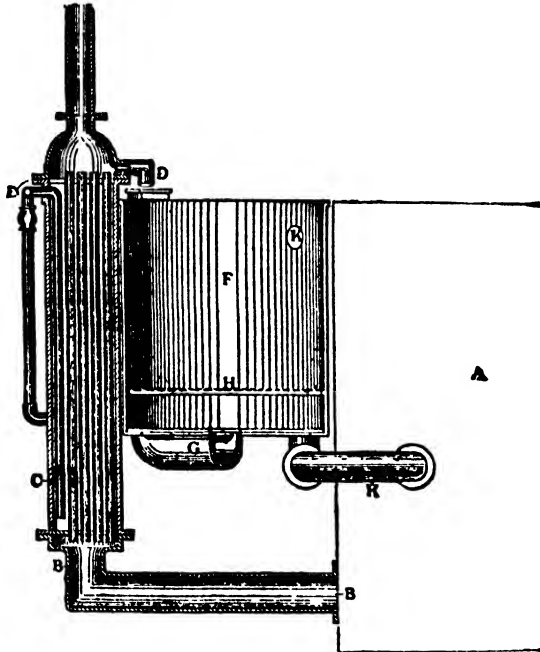


Fig. 105.—Smithson's dyewood extractor (section).

extracting vessels, F, constructed of cast iron, and provided with false bottoms, H, which are attached to the side of the dye-vessel, A. From a point a few inches above the bottom of the dye-vessel there passes a pipe, B, which has a through connection with the nozzle, D, through a number of tubes or pipes shown in the figure. These pipes are enclosed in a steam-tight cylinder, C, into which high-pressure steam is admitted when the machine is in operation. The dye-liquor in the vat finds its own level in the tubes connected with B, and, becoming here heated to boiling, the liquid expands, and rising above the flange, E, finds an outlet at D, and empties itself into the pipe, G. The boiling liquor passes down the pipe, G, and, entering the extractor at the bottom, rises slowly until it reaches the point, where it passes out and back into the vat again through the pipe, K. Sieves prevent bits of dyewood getting into the pipe, K. A continuous circulation is thus established, by means of which the wood is completely extracted. Two extractors are provided, so that while one is being used, the other can be emptied and refilled.

In large works the dyewoods (principally logwood and fustic) and tannin

substances are sometimes extracted in large wrought-iron extractors, and the liquors are conducted by means of pipes from the reservoirs in which they are stored, into the dye-house. The system is both convenient and economical.

**Operations after Dyeing—Steaming.**—In textile printing this is a most important operation, as most of the colours are fixed in this way, But in dyeing, steaming is only made use of in one or two special cases, as in the production of Alizarin reds, Turkey red, and Aniline black (*q.v.*).

**Washing.**—After mordanting or dyeing, the goods are usually washed in water for the purpose of removing the excess of mordant or dye-solution which they mechanically retain. This is necessary after mordanting in order to prevent any of the mordant getting into the dye-bath, for if this occurred, some colour would be lost through the formation of an insoluble lake in the dye-bath and not on the fibre. After dyeing, washing-off is generally necessary in order to cleanse the material from excess of colour and additions to the dye-bath.

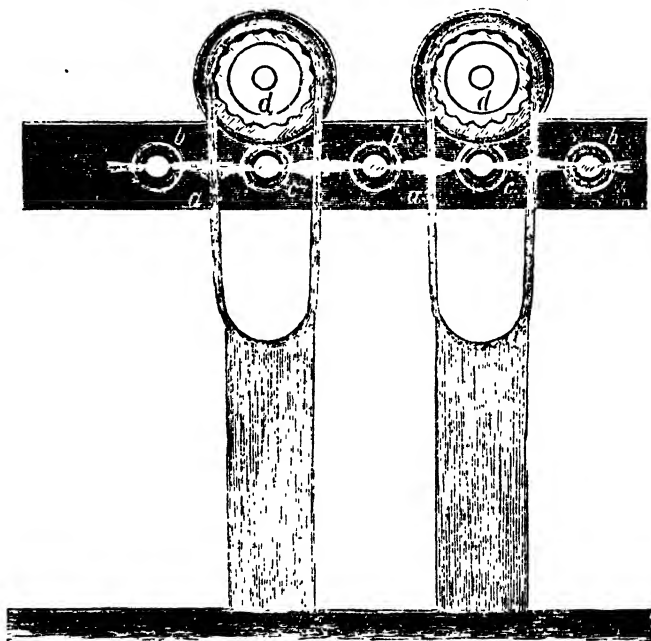


Fig. 106.—Hank-washing machine (details).

In some cases, as in the mordanting of silk with tin or iron, the washing-off has besides the effect of fixing the mordant.

The operations of washing and the construction of washing machines have already been dealt with under the heading Washing and Bleaching, and most of the machines described there could be used equally well for washing off after mordanting or dyeing.

**Loose Fibre.**—The washing of loose fibre is generally done in the vessel in which it has been mordanted or dyed by letting off the liquor and stirring after having filled with water, the operation being repeated several times.

**Yarn.**—The washing of yarn has hitherto generally been done by hand. In the form of *hanks*, yarn is simply rinsed in clean water, two or three turns being, as a rule, sufficient. If running water is at hand it is certainly preferable to washing in a vat or tub. Worsted yarn or slubbing is "showered"

after mordanting or dyeing by running a stream of water over the material suspended on rods resting upon a wooden frame, through a large sieve.

Since much labour is required in washing by hand, many machines have been constructed to replace hand labour, and of these some are quite capable of doing so. One of the most effective of such machines is that constructed by Berchtold (Thalwyl, near Zurich). Fig. 106 shows a section of two of the rollers.

The machine consists essentially of a double row of porcelain rollers, *d*, on which the hanks to be washed are suspended, and which receive, through the gearing at one end of the machine and the worm-gearing in the boxes an alternate backward and forward motion. Whilst the hanks, *a* (Fig. 106), are being thus turned backwards and forwards, they are thoroughly washed by jets of water which emanate from the perforated pipes, *b* and *c*, placed so as to come alternately inside and outside of each hank. In some machines, similarly constructed, the water emanates from perforations in the porcelain rollers.

Yarn in the *warp* is washed in the same machines as those employed for mordanting and dyeing.

*Pieces.*—The washing of pieces is almost invariably done by machinery. Several machines for this purpose have already been described under Washing and Bleaching (*q.v.*). For woollen and worsted goods the dolly and broad-washing machine are mostly employed. Several of the piece-dyeing machines (*e.g.*, the jigger) described may also be used for washing-off. Another form of washing machine used specially in the washing of cotton pieces is the so-called square-beater washing machine described under Bleaching (pp. 104 and 105).

The pieces, stitched together end to end, pass into the machine in rope form and, following the course indicated by the arrows in the section, pass first round the winch roller, thence through the squeezing rollers, past the square beater, through the water back to the winch roller, following the same course over and over again in a spiral direction until they leave the machine at the other end, and are drawn off by the winch. In passing the square beating roller (shown in the section as being driven by spur gearing from the squeezers, while in the view it is driven direct from the fast pulley, the squeezers in this case being driven by spur gearing), which revolves in a contrary direction to that followed by the pieces, the cloth opens out from the rope form to almost its full width in passing underneath and along the surface of the water, and receives at the same time a flapping motion. The washing is thus done at a high speed, and at the same time very effectively.

**Removal of Mechanically-absorbed Water.**—When wetted out, all textile fibres (whether in the loose state, as yarn, or in the piece) mechanically retain considerable quantities of water through capillary attraction. After washing and previous to drying, it is advisable to remove the mechanically-absorbed water as completely as possible; indeed, this is imperative if the drying is to be done rapidly and economically. For, taking into account the large amount of heat which becomes latent (and is thus lost for all practical purposes) in the evaporation of the water in drying, it is at once apparent that the most efficient mechanical means for removing the water will produce the greatest economy in drying.

The mechanical removal of liquid from textile materials is principally effected in three ways, *viz.*, by

1. Wringing.
2. Squeezing.
3. Hydro-extracting.
4. Suction by vacuum.

The following interesting account of the results of a series of comparative



trials with the first three methods named has been published by Grothe.\* The figures given indicate in percentages (of the total absorbed) the amount of water removed (in the case of hydro-extracting in fifteen minutes):—

		Wool.	Silk.	Cotton.	Linen.
For pieces.	{ Wringing, . . . . .	44.5	45.4	45.3	50.3
	{ Squeezing, . . . . .	60.0	71.4	60.0	73.6
	{ Hydro-extracting, . . . . .	83.5	77.8	81.2	82.8
For yarns.	{ Wringing, . . . . .	33.4	44.5	44.5	54.6
	{ Squeezing, . . . . .	64.0	69.7	72.2	83.0
	{ Hydro-extracting, . . . . .	77.8	75.5	82.3	86.0

A comparison between the effectiveness of squeezing and hydro-extracting, respectively, as a means of removing mechanically-absorbed water from cotton pieces is given by Riesler.† Six pieces of wet calico which had been through the squeezing rollers weighed 47.5 kilos. After being treated in the hydro-extractor, the same pieces weighed only 39.25 kilos. From this he calculates that for 100 pieces, 138 kilos. more water could be mechanically removed by hydro-extracting than by squeezing, which would mean for this quantity of material a saving, in the subsequent operation of drying, of 50 to 75 kilos. of coal.

1. **Wringing.**—This method is employed almost exclusively for hanks. The hanks are suspended on a rod or peg (generally fastened with one end into the wall), and twisted up tight by means of a short stick. They are then unwound, turned a quarter round and wrung or twisted again. Sometimes, as is, for instance, the case in sizing hanks, or in mordanting with oil for Turkey-red dyeing (p. 584), the wringing is done by machinery.

2. **Squeezing.**—Squeezing is employed for loose fibre, yarn, and pieces. The operation simply consists in passing the materials between two rollers, one of which runs in rigid bearings, while the other (generally the upper one) is pressed against it by means of springs or weighted levers.

Squeezing rollers are employed in many of the dyeing and washing machines already described. A convenient form for yarn especially used by silk dyers is that shown in Fig. 107. It consists of two india-rubber rollers geared together by spur-wheels. The pressure is exerted by spiral springs, and the machine is so constructed that it can be affixed to any dye-vat of ordinary breadth.

For the squeezing of woollen pieces in rope form, a machine is employed like that shown in Fig. 108, constructed by C. W. Tomlinson of Huddersfield. The pieces pass through the eye shown in the figure and between the squeezing rollers, which are geared together by spur-wheels, the pressure being imparted by weighted levers to the upper one. The top roller, which is plain, fits into the rut of the lower one, and the liquid is thus expressed by top as well as by lateral pressure.

3. **Hydro-extracting.**—The hydro-extractor or centrifugal machine most in use consists essentially of a circular cage of strong galvanised iron wire or of perforated sheet copper, which is caused to revolve horizontally at a rapid rate around its centre. Any substance, the surface of which presents sufficient friction to be carried round by the cage is pressed against its periphery, and the quicker the cage revolves the greater will be the pressure exerted. If a piece of wet material is placed in a hydro-extractor and the latter is set in motion,

\* *Appretur der Gewebe*, 1882, p. 616.

† Herzfeld, *Das Färben u. Bleichen d. Text. Fas.*, II., p. 288.

the material is thrown by the centrifugal force against the sides of the vessel. The openings in the side of the cage being too small, the material cannot escape, but the water which it mechanically retains. will continue to pass

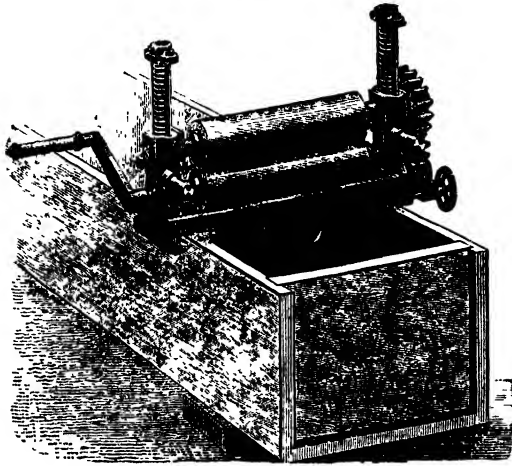


Fig. 107.—Yarn squeezing rollers.

through the sides of the cage until the centrifugal force is equalled by the force of capillary attraction of the material. The cage is surrounded by a cast or

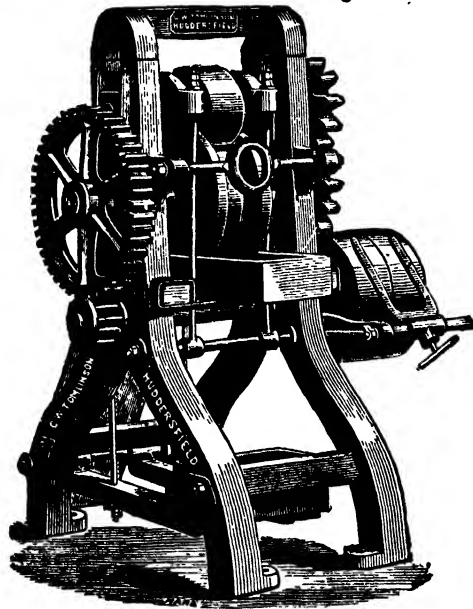


Fig. 108.—Squeezing machine for woollen pieces.

wrought-iron casing against the sides of which the water is thrown, whence it trickles down and flows off at the bottom.

The hydro-extractor is used for all classes of textile material, and is

constructed in a great variety of forms, which differ chiefly in the mode of applying the motive power required for causing the drum to revolve.

When the cage is unevenly balanced the hydro-extractor has a tendency to oscillate. To overcome this difficulty the whole machine is usually firmly fixed to a very solid foundation, and care is taken in putting the goods into the cage to lay them as evenly as possible all round. In many of the hydro-extractors of more recent construction all vibration is done away with, either by causing the cage to run in elastic bearings, or by suspending the whole machine on three columns, which are not rigid, but give slightly with the oscillatory movement of the machine. Fig. 109 shows an under-driven hydro-extractor of the latter description, with engine attached, constructed by Broadbent of Huddersfield. Two of the columns, C, on which the machine is suspended are visible in the figure.

Non-vibrating hydro-extractors working on the principle of elastic bearings (Weston's patent) are constructed by Messrs. Watson, Laidlaw & Co., of Glasgow.

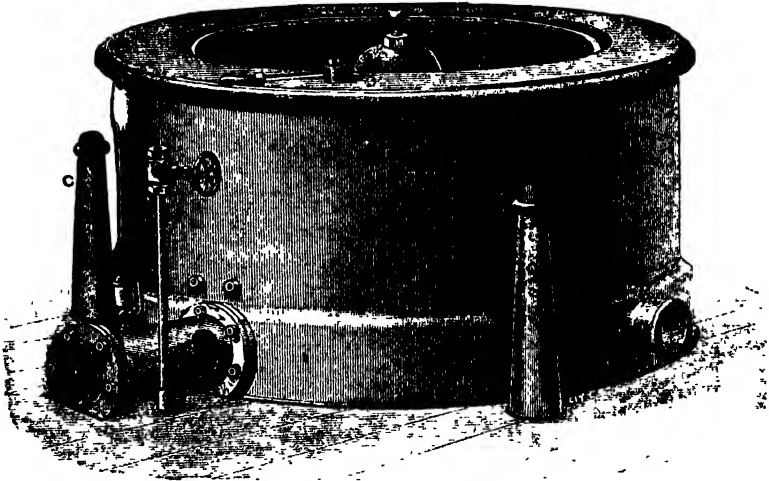


Fig. 109.—Broadbent's hydro-extractor.

Quite another form of hydro-extractor, used principally for pile fabrics and sometimes for worsteds, is that shown in Fig. 110.

It consists of a drum, D, which can be caused to revolve at a high rate of speed, and round which several pieces stitched together end to end are wound at their full breadth. The drum is surrounded by a casing, C, which is provided with a lid, L, which remains closed while the machine is working. In its action this form of hydro-extractor is similar to those described above, the main difference being that here the material is caused to revolve around a horizontal shaft, while in the others the shaft is vertical. After the operation is over the pieces are either drawn off and plaited down, or batched on a roller, R.

There appears to be no doubt that the hydro-extractor is the most efficient means yet devised for the removal of mechanically-absorbed water from any class of textile material. As it is, it is used largely in dye works, especially for materials which might be damaged by squeezing rollers. But its employment would probably be considerably extended if it could be made to turn out more work in a given time than is at present the case.

4. **Suction by Vacuum.**—The suction device for removing excess of water from piece goods which is specially suited for light fabrics consists essentially of a hollow chest which communicates with a vacuum pump. On the top of the chest there is a slit, about one-eighth of an inch in diameter, over which the pieces pass. By means of dampers, the length of the slit may be varied to suit the width of the piece. For many classes of goods this method of removing excess of water is preferable to the use of the hydro-extractor and is, moreover, much more rapid.

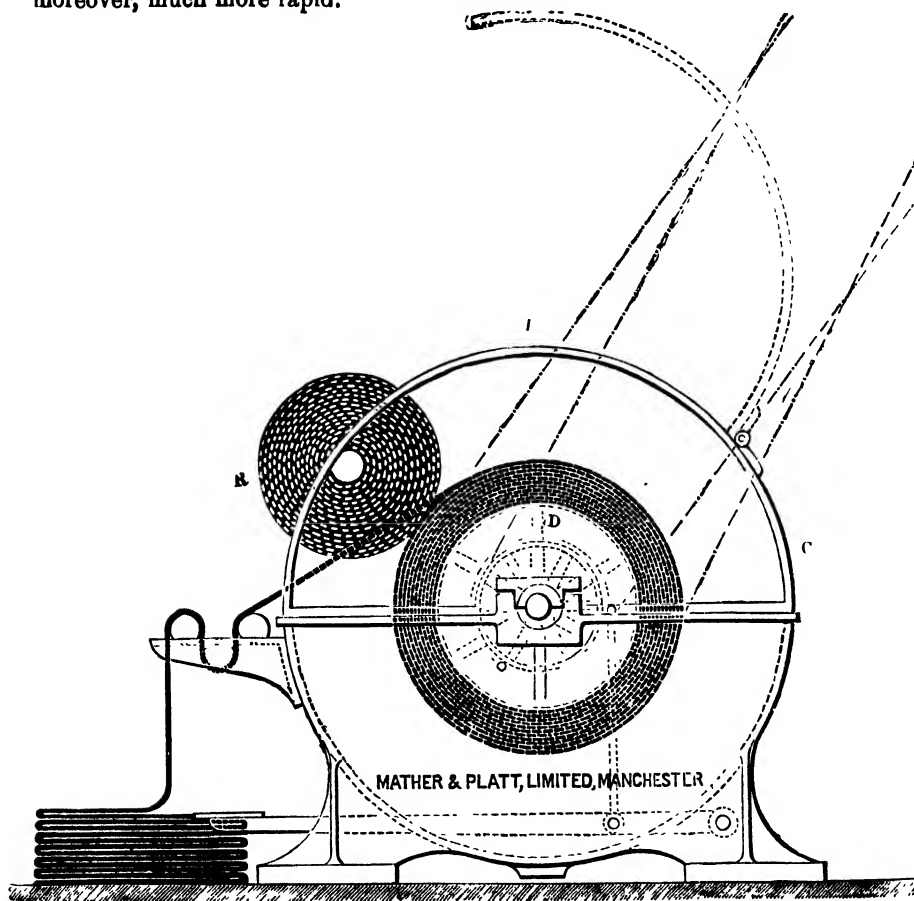


Fig. 110.—Hydro-extractor for pile fabrics.

**Drying.**—The simplest means of drying is to expose the material, after it has been wrung, squeezed, or hydro-extracted, to the open air. This method of drying slowly, and at a low temperature, is certainly economical where plenty of space is available, and where time is no object; at the same time, the brilliancy of certain colours is thus preserved, and the material, when dry, is in proper condition—i.e., it contains about the normal amount of hygroscopic moisture.

But in the majority of works the drying is done almost exclusively by artificial means, partly because the necessary space for air-drying is not available, but more especially because it is necessary to get the goods out as rapidly

as possible. This is prevented in natural drying by the slowness of the process, *per se*, on the one hand, while, on the other hand, considerable delay might result from inclement weather.

*Loose Fibres.*—The machines employed for the drying of loose fibre call for no special description. The material, after having been squeezed or hydro-extracted, is spread out evenly on a flat surface of galvanised iron wire netting, and a current of hot air is blown through by means of fans. Machines are also constructed on the counter-current system, in which the material is carried by an endless chain through the machine, meeting on its way a current of hot air. In the machine of M'Naught (Rochdale), specially designed for the drying of loose wool, the material is fed in at one end of a large revolving cylinder, which is placed at an incline, so as to cause the wool to roll slowly to

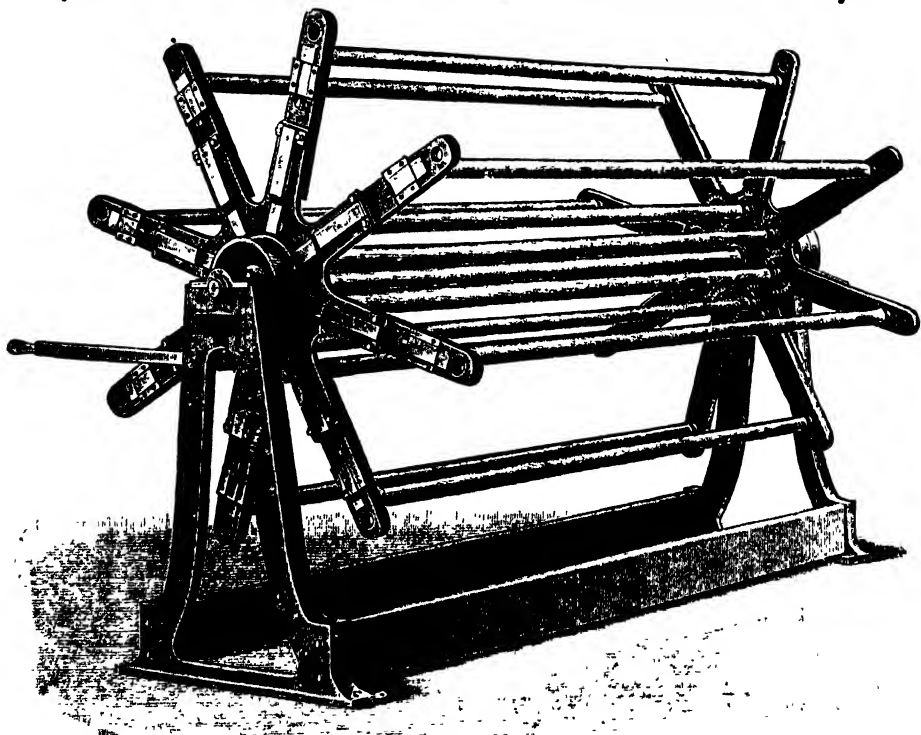


Fig. 111.—Haubold's yarn-drying machine.

the other end. In its passage through the cylinder it meets a current of hot air, and is delivered at the other end dry.

In the Obermeier system of dyeing (p. 698) the dyed loose wool or cotton, after having been hydro-extracted, is either dried in stoves or is put back into the dyeing machine, and dried by forcing a current of hot air through the machine. A similar principle is adopted in the drying of tops and cops which have been dyed by machinery.

*Yarn.*—Yarn in the hank is generally dried by suspending the hanks on poles in drying stoves. The stoves, through which a slow current of air is maintained, may either be heated by steam-pipes, or the air may be heated in this manner before entering. In many works, the drying stove is placed immediately above the works' boilers, and having a perforated or

trellis iron floor, it receives the hot air which rises from the surface of the boilers.

Drying stoves are sometimes constructed in such a manner that the sticks or poles holding the yarn are suspended on a framework which, when filled with yarn, is run into the stove. When the yarn is dry the framework is withdrawn and the yarn taken off.

Hank-drying machines are also constructed, in which the hanks suspended on sticks are carried by two endless chains through the machine, and, meeting in their passage with a current of hot air, are delivered at the other end in a

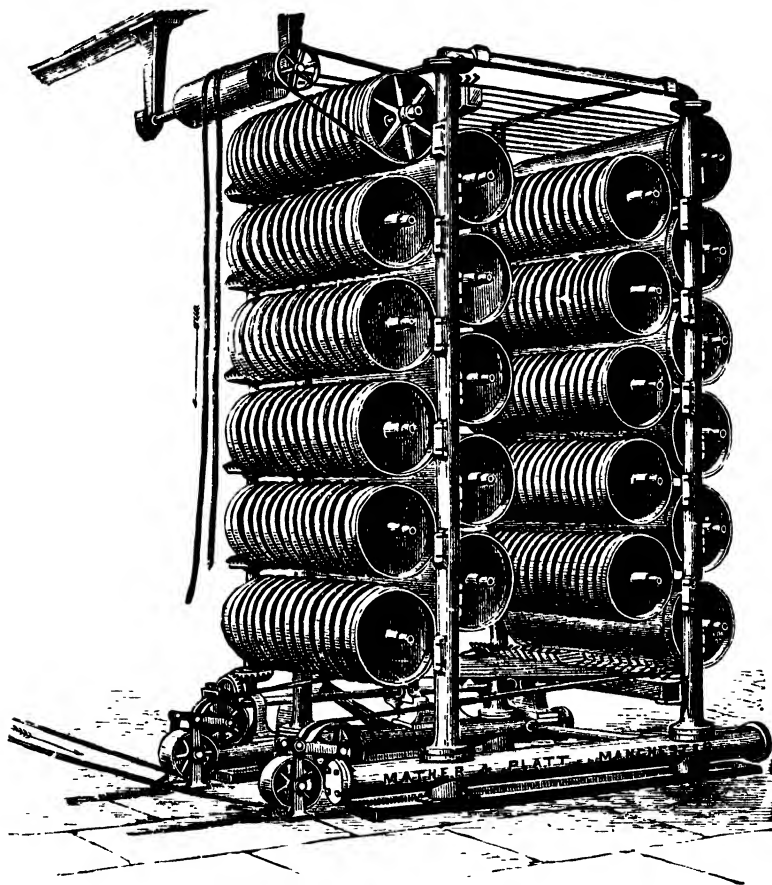


Fig. 112.—Warp drying machine.

dry state. Machines of this kind act more rapidly than drying stoves, and are, perhaps, more rational than the latter; but hitherto they have not been introduced to any great extent into works, probably on account of the initial expense.

A hank-drying machine, by means of which the drying may be achieved at the ordinary temperature, is constructed by C. G. Haubold, jun., and is shown in Fig. 111.

The hanks are suspended from the cross-bars near the axis to those at the periphery, and the machine is set in motion. At the same time the cross-bars near the axis revolve, and the hanks are thus slowly turned as they are carried

round. By means of a machine of this kind, yarn, which has been properly hydro-extracted, can be dried at the ordinary temperature in one to two hours, and has, after drying, a soft and full feel and a bright appearance.

Warps are usually dried on steam cylinders. A warp-drying machine, with two vertical sets of drying cylinders, is shown in Fig. 112.

The warps enter at the bottom, and, after passing round all the cylinders

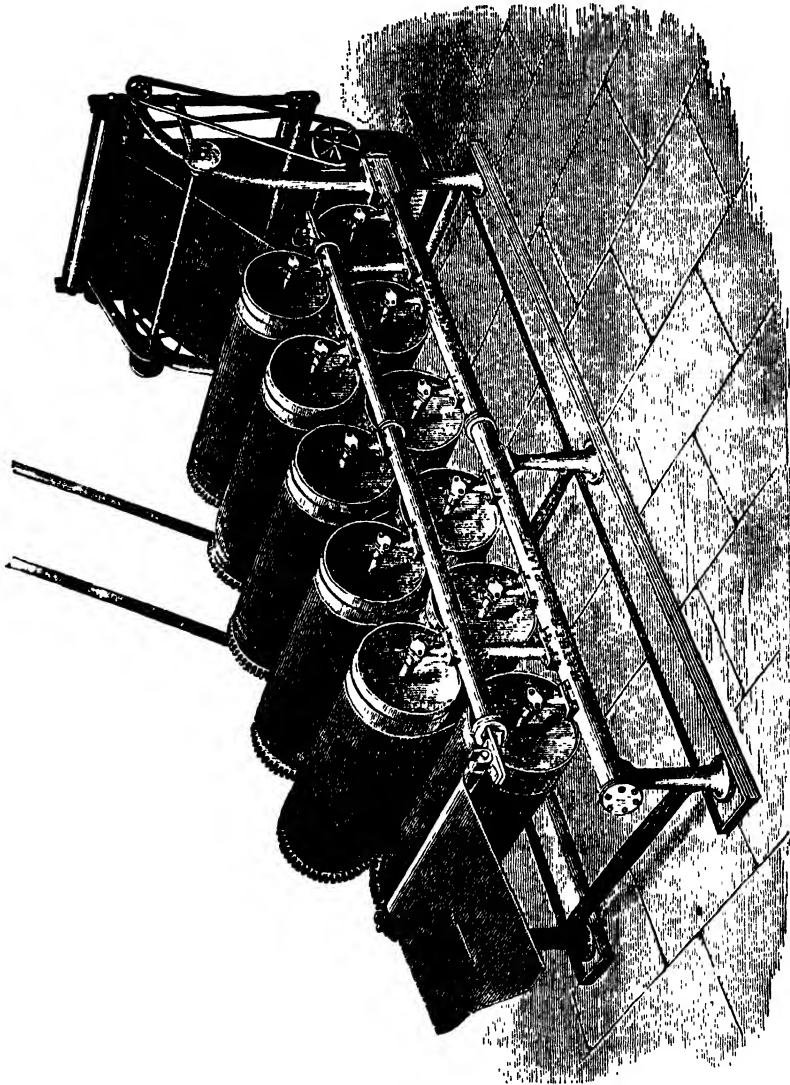


Fig. 113. — Horizontal piece-drying machine.

several times, are delivered dry at the top, as shown by the arrows. The cylinders, which are made of copper or tinned iron, are heated by steam.

For the drying of cops and cheeses, hot air may be forced or drawn through the material on the machine, but the plan usually adopted is to dry in the stove. Warps dyed on the beam may be dried on the beam or over cylinders.

*Pieces.*—Dyed pieces are almost invariably dried on steam cylinders. A horizontal piece-drying machine, consisting of eleven tinned iron or copper cylinders, geared together by spur-wheels and heated by direct steam, is shown in Fig. 113.

The course which the pieces follow in passing through the machine is distinctly shown in the figure, and requires no further explanation. This machine contains 11 cylinders; machines are now frequently constructed with 30 or even more cylinders, which naturally do the work very much more rapidly.

Some piece-dyers prefer to use vertical drying machines, chiefly on account of their requiring less space. The steam pressure in the cylinders of either form of drying machine does not usually exceed 10 lbs. per square inch.

The cooling action of the wet pieces passing over the drying cylinders naturally causes a considerable amount of water to condense in these, and this is removed automatically by means of an arrangement like that shown in Fig. 114, in which the water is caught in three scoops or "buckets" and delivered through the hollow axis opposite to that through which the steam enters.

For opening out the pieces and getting out all creases before they pass on

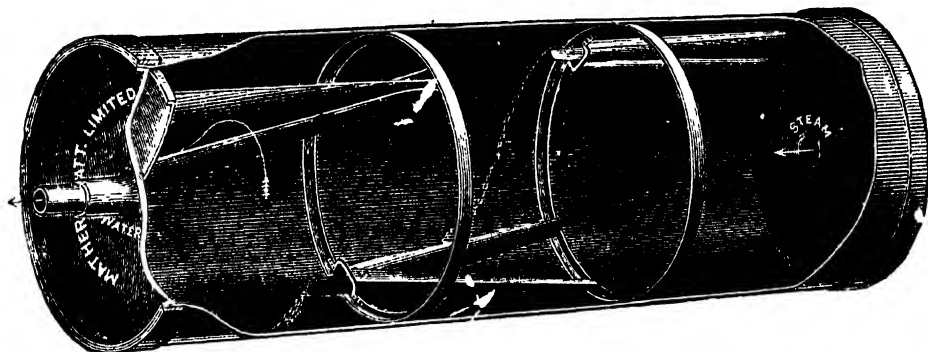


Fig. 114.—Bucket system for collecting water condensed in drying cylinders.

to the drying cylinders, several devices are in use. The simplest means is the so-called *scrimp-rail*, which consists of a brass rail with incisions diverging from the centre.

An ingenious and effective arrangement for this purpose is that constructed by Messrs. Mather & Platt, and shown in Fig. 115.

Before passing on to the first drying cylinder, the pieces pass over two conical rollers, A A, on each of which a screw-thread runs from the thin to the thick end. The rollers are placed at such an angle to each other that the pieces, as they pass over them, are drawn on each side from the centre, and thus become straightened out. For the purpose of keeping the pieces to the middle of the drying cylinders, the frame-work in which the rollers run is attached to the rail, R, by a swivel joint, S, which is allowed a certain amount of play. If the piece begins to run on one side, it gets on to the thick end of the expanding roller on that side, and presses the latter against an india-rubber brake, a. The other roller, running free, draws the piece towards the other side, thus relieving the brake, and the pieces are in this manner not only kept straight but are forced to remain in the middle of the cylinder.

For the drying of pile-fabrics, it is essential that the pile should not be pressed against the hot surface of the cylinders, as it would thereby be



damaged. Such materials are either dried in stoves or on the back only by an arrangement like that shown in Fig. 116.

After passing over the first drying cylinder, the pieces pass with the face side over wooden rollers, then on to the next drying cylinder, and so on through the whole machine—always with the face away from the cylinder.

In the dyeing of pieces, the various operations through which the material has to pass almost invariably cause a certain amount of shrinkage in breadth. In order to get them to the original breadth again, they are *stretched*, *tentered*, or *stentered*. The stretching or tentering machines used for this purpose vary considerably in their construction. The principle most generally adopted is to feed the wet or moist pieces at full breadth into the machine, where they are

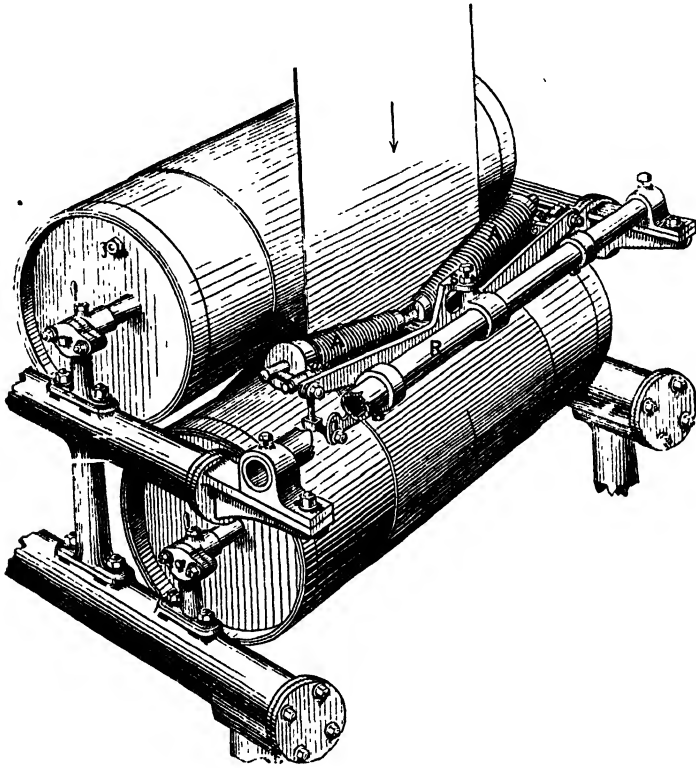


Fig. 115.—Conical opening rollers.

seized at the selvages by pins or clips borne by two endless chains which run along the whole length of the machine. The chains run in slotted frames and are not parallel, but diverge slightly from the feeding and towards the delivery end, and the pieces held by them are thus widened out to the desired degree. When they arrive at about the middle of the frame, heat (gas or hot air) is applied from beneath so that the pieces are dry on leaving the machine. Fig. 116 shows the appearance of a machine of this kind. The chains here carry clips, and the heating is done here by flanged steam-pipes. By a simple contrivance the distance between the two chains may be altered to suit the width of the material to be tentered.

Another form of stretcher in which the chains carrying the clips travel in



Fig. 116 - Stretching or stentering frame

a vertical plane is shown in Fig. 117. Stentering frames vary in length from 40 to 100 feet.

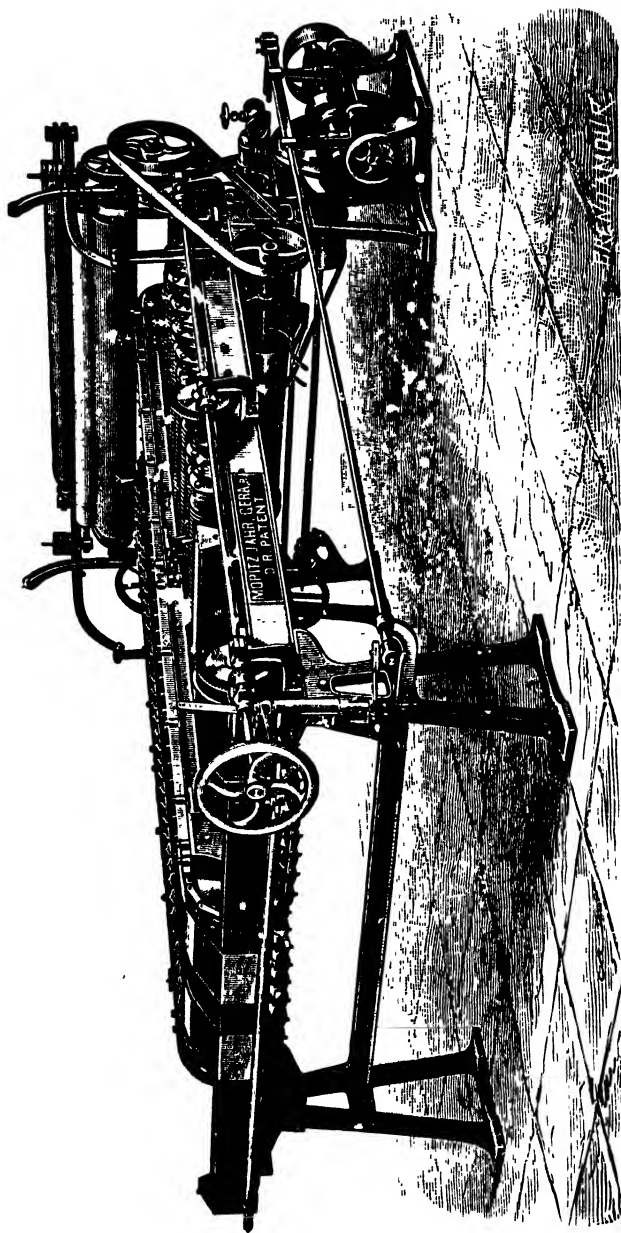


Fig. 117.—Stentering machine.

## PART X

## EXPERIMENTAL DYEING AND FASTNESS OF DYED COLOURS.

By means of experiments carried out on the small scale and systematically conducted, it is possible for the dyer to gain a large amount of useful information which cannot well be obtained in the works, owing to the time and expense which similar experiments would involve if carried out on the large scale. Most of the new colouring matters, mordants, &c., which now come into the market are accompanied by more or less reliable recipes from the makers. But suppose, for instance, that a new colouring matter comes into the hands of a dyer with no further information than that it is a dye, he must necessarily have recourse (if he wishes to use it) to a series of experiments in order to find out whether it is more suitable for wool or for cotton, whether it requires a mordant or not, and then, having found the best mode of applying it, by more careful experiment, to determine its strength, its value, as compared with that of known dyestuffs which dye a similar shade, and its fastness to light, milling, and other influences.

Whether the colour be a *direct cotton dye* or not, is readily determined by boiling a small swatch of cotton in the aqueous solution of the dyestuff, to which a small amount of soda or soap and salt has been added, for about 10 to 15 minutes. If the cotton thus treated retains a full colour after washing well with water, the dye is a direct cotton dye. Such an indication would at once determine the course of subsequent experiments. If the colour is one which would be most serviceable for the production of compound shades with the other known direct dyes, it will be best to determine its strength and relative price by dyeing it on cotton by one of the methods generally employed for the direct dyes (see p. 381). But if the colour should be of such a character as to render it more useful for self-colours (as is, for instance, the case with Erika and Benzopurpurin), a series of experiments will be necessary in order to determine by comparative dye-trials the most favourable conditions as to time, temperature, concentration, additions to dye-bath, &c., for its application. The experiments might be conducted in the following order:— Three dye-trials are made with, say, fifteen, thirty, and sixty times as much water (by weight) as material in the dye-bath (for 10 grms. of cotton, 150, 300 and 600 c.c.), using say 2 per cent. of colouring matter in each case, and dyeing for one hour at 100° C. in an ordinary 6-hole experimental dye-bath. Cotton yarn will be found most convenient for such experiments. After dyeing, the hanks are taken out, rinsed, dried, and compared with each other. It will probably be found that that which has been dyed in the most concentrated liquor has the deepest colour, and this degree of concentration should, strictly speaking, be adhered to in the subsequent experiments. For piece dyeing even greater concentrations would not be disadvantageous, but for yarns, one in which twenty times as much water as cotton is taken is most in accordance with practical working, and this is taken as the standard amount for subsequent experiments. Next would come experiments for the purpose of testing the effect of additions to the dye-bath, first of acids and alkalis,

and then of neutral soluble salts. Of acids one might try the effect of oxalic and acetic in amounts varying from  $\frac{1}{2}$  to 2 per cent. of the weight of the cotton, and of alkalies, such as sodium carbonate, potassium carbonate, sodium phosphate, borax, soap, of each 1 to 10 per cent. After having determined which alkali or acid gives the best result, and what amount is to be used, the effect of neutral soluble salts added to the dye-bath might be determined. Such salts as Glaubersalt and common salt have the effect of diminishing the solubility of most dyestuffs in water, and, in the case of direct cotton dyes, cause more to go on and into the fibre. Of common salt, the effect might be tried of say, from 2 to 50 per cent. Stannate of soda, aluminate of soda, and, more especially, Turkey-red oil and soda, frequently have the effect of producing brighter colours when added to the dye-bath; their action should, therefore, also be tried. If the water in the dyeworks is hard, a hank should be dyed in that water and compared with another dyed under similar conditions in distilled water in order to determine whether the hardness causes any loss in colouring matter in consequence of the colour forming an insoluble calcium salt. If this is the case, the water should be softened or corrected before use. The effect of time and temperature in dyeing is now soon determined, by dyeing, say, three skeins each with the same amount of dyestuff for 15, 30, and 60 minutes at the boil, and another set for one hour each cold, at 50° C. and boiling respectively. Most of the direct cotton colours and sulphide colours do not exhaust well—i.e., a considerable proportion of the dyestuff employed remains in the dye-bath, however long the dyeing may be continued. If the bath is kept and the same amount of dyestuff is added for a second lot of cotton as was used for the first, it is evident that a darker shade will result. Exhaust experiments should, therefore, be made in order to determine what amount of colour is left in the dye-bath and how much is fixed on the fibre, as well as to ascertain what quantity is necessary for obtaining the same shade on the second and subsequent lots of material as on the first. Another important point which should not be left untried is to determine whether raw cotton, boiled cotton, or bleached cotton gives the best result in dyeing. For very light and brilliant shades the employment of bleached cotton will be inevitable, but for full shades raw or boiled cotton will generally be found to give better results.

If the colour under examination be a *sulphide colour* this will be recognised by the fact that, after acidulating and boiling, it loses its solubility in alkalies. To completely dissolve the colour it will probably be necessary to employ a solution of sodium sulphide. In this solution cotton will be dyed without additions. As in the case of the direct cotton colours, it will, however, be advisable to carry out systematic comparative dye-trials in order to ascertain the effects of concentration of dye-bath, time, temperature, and additions to the bath of sodium sulphide, Glaubersalt, soda, &c., and also to ascertain by exhaust trials to what extent the colour is taken up in the first bath. In some cases—e.g., with blacks—it may be found advantageous to add only a portion of the Glaubersalt at the beginning of the dyeing operation and the rest after the dyeing has proceeded for, say, half an hour. Some of the sulphide colours are improved by a treatment, after dyeing, with oxidising agents. The effect of many of these might be tried, but, as a rule, it will suffice to ascertain the effect of treating the dyed cotton with bichromate and acetic acid.

If the colour under examination be a *basic dye*, it will dye wool and silk, without any further addition, a full shade, but will probably only tinge the cotton. If to its aqueous solution there be added a solution of tannin and sodium acetate, an intensely coloured precipitate will result. Such a colouring matter might be suitable for both cotton wool and silk dyeing, but the former would have to be mordanted first by one of the known methods. Experi-

ments might be conducted by dyeing it on cotton mordanted with different percentages of tannic acid in the first place, in order to determine what proportion of the latter is most suitable for a given percentage of colour. Having obtained this result, one might try the effect of fixing the tannic acid by antimony mordants, stannous on the cotton previous to dyeing, or stannic chloride, aluminium or chromium acetate, or, if dark shades are required, with an iron mordant. The effect of time, temperature, and concentration of dye-bath could be determined as in the foregoing example of the direct cotton colour.

If it is a question of an *acid dye*, the cotton will only be tinged and the wool dyed, as a rule, a somewhat meagre shade, or perhaps not at all in a neutral bath, but on the addition of a little sulphuric acid to the dye-bath, the colour will probably be rapidly absorbed by the wool and the dye-bath more or less completely exhausted.

Such a dyestuff is practically of no use for cotton, but may be valuable on wool or silk. It will probably have been gathered from the preliminary experiment that no good results are obtained in a neutral bath, and a single experiment will suffice to show that the addition of only a small quantity of alkali prevents the colour from combining with the fibre. When dyed in an acid bath at the boil it will probably be seen that the colour is taken up very rapidly, and the bath is almost completely exhausted. If the colour produces a level and bright shade in this manner, and at the same time exhausts the bath, nothing further will be necessary than to determine, by comparative dye-trials, the best amount of acid to be used. But it frequently happens that the acid dyes are very prone to produce uneven or speckled effects on wool. Several methods might be tried in order to obviate this fault. In the first place, it would be advisable to try the effect of adding some soluble salt, such as Glaubersalt, along with the necessary acid, to the dye-bath; as a rule, this has the effect of causing the dyeing to take place more slowly and more evenly. The amount employed in the comparative experiments might be made to vary from 5 to 50 per cent. of the weight of the wool. In place of sulphuric acid and Glaubersalt, the use of sodium bisulphate might be tried. Should the colour still dye unevenly, the effect of an addition of ammonium acetate or ammonium sulphate to the dye-bath should be tried. It might be found that by boiling the wool first with a small amount of sulphuric acid (2 to 10 per cent.), or with alum and tartar, and subsequently dyeing in a neutral bath, better results would be obtained. Further experiments might show that better results are obtained by entering the wool into the dye-bath cold, and heating gradually to the boil, or by adding the colouring matter, or the necessary amount of acid, to the dye-bath, not all at once, but in small portions at a time, or by using one of the methods indicated on p. 513. It might be that under all these conditions the dye evinced very little affinity for the wool, as is for instance the case with the Indulines. In such a case it would be advisable to try the effect of chlorinating the wool before dyeing (see pp. 58 and 551).

If the colouring matter dyes neither wool nor cotton, or if it only produces very inferior shades when applied in a neutral, alkaline, or acid bath, it is probably a *mordant-dye* or a *vat-dye*. Whether this is the case or not, is readily determined by boiling a piece of stripe-mordanted calico (mordanted in stripes with alumina, iron, and chromium) in the neutral dye-solution. If it was a mordant-dye, the three stripes may possibly be dyed in different shades, and of these the best may be taken for further experiments. Copper and tin mordants, fixed according to methods described on pp. 285 and 276, might also be tried on cotton. Some mordant-dyes yield very poor shades on simple mordants, and if the results obtained on the stripe-mordanted calico are not good, the use of compound mordants, such as chromium and zinc (see p. 253), alumina and stannous

oxide, alumina and lime, iron and lime, might be tried (see pp. 573 and 576). An addition of lime salts to the dye-bath in the form of calcium acetate or chalk will often be found to give beneficial results.

In place of dyeing the mordanted cotton, it might be found better to reverse the operations—*i.e.*, to pad boiled or bleached calico in the solution or decoction of the dyestuff, and afterwards develop the colour by passing through hot or cold solutions of alumina, iron, chromium, or copper salts.

In some cases the brilliancy of the dyed colour is considerably improved by steaming under pressure.

On wool, the course of experiments would be somewhat different to those conducted on cotton. By far the most important wool mordant being bichromate of potash or soda, this would be tried first. Three lots of wool mordanted respectively with bichromate of potash, with bichromate and sulphuric acid, and with bichromate and tartar would be dyed under similar conditions with equal percentages of the dyestuff and the results compared. In some cases (as for instance with Gallein), very great differences in shade might be observed in this experiment. Other mordants, such as alumina, iron, copper, and tin fixed on the wool by the methods already described, might also be tried. Possibly better results might be obtained by stuffing and saddening—*i.e.*, by boiling the wool, first, with the colouring matter, taking of course the same percentage as used by the mordanting and dyeing method, and then developing in the boiling solution of some metallic salt, such as alum, copperas, copper sulphate, or bichromate. Good results might also be obtained with one or more of the different mordants by the single-bath process, as is, for instance, the case with cochineal and flavin in conjunction with a stannous salt. Should this be the case, one operation—*viz.*, that of mordanting—could be dispensed with, and if the dyestuff could be used along with others which also dye on the same mordant, a considerable saving in expense might thus be effected. In the dyeing of the acid chrome colours, the bichromate is added to the bath after dyeing. The best amount to be added should be ascertained; while the effects of chrome alum, chromium fluoride, copper sulphate, &c., might be compared with those obtained with bichromate.

If it is intended to use the dye for silk, similar experiments could be made to those carried out on wool. If the colour dyes silk directly, the effect of alkaline boiled-off liquor on the one hand and of acidulated boiled-off liquor on the other should be tried in dyeing. After dyeing, the effect of brightening in a weak solution of tartaric acid should be tried.

In case the colour is a *vat-dye* it will be insoluble in water, dilute acids, and alkalies, but will be reduced by hydrosulphite of soda in presence of caustic soda to a soluble leuco-compound, and from this solution cotton will take up the colouring matter which, on exposure to the air, will assume its true shade. With a *vat-dye* experiments might first be conducted with a view of finding out the most suitable reducing agent—hydrosulphite of soda, sodium sulphide, zinc and lime being tried for the purpose. The effect of excess of caustic soda, salt, &c., in the vat should be studied, and it should also be ascertained at what temperature the best results are got and to what extent the bath is exhausted. Some *vat-dyes*, like indigo, exhaust badly, while others, like tetrabromindigo, completely exhaust the vat.

In any case, a subsequent treatment of the colour dyed on the fibre, in different chemical agents, such as bichromate of potash, salts of copper, iron, &c., may bring about a useful alteration in the shade or may improve the fastness of the colour. Thus, catechu is developed in bichromate, Aniline black is rendered ungreenable, and the magenta colour of Chromotrop on wool is turned to a full black by this treatment. Alkali blue dyed on wool in a neutral bath only shows its full colour after being passed through a hot dilute solution of acid.

A treatment with an emulsion of oil in soap, or with a solution of neutralised Turkey-red oil, wringing and drying without washing, often has the effect of enhancing the brilliancy of colours dyed on cotton. Again, the direct cotton colours are rendered faster to light by treatment in boiling copper sulphate subsequent to dyeing, or may be subjected to diazotising and developing or to a treatment with diazotised *p* nitraniline, &c.

## FAST AND LOOSE COLOURS.

The term *fast*, as applied to the colour of dyed materials, usually implies, in the first place, that the colour will withstand the action of *light*, and, in the second place, that of *washing*. Fastness to light and washing are the principal, but not the only, desiderata of a good colour.

Fastness to *acids* is also frequently required, especially in cotton warps intended for cross dyeing, in wools which are carbonised after dyeing, and in dyed materials which are worn next to the skin, and which should not be affected by the organic acids contained in the perspiration. In large towns where much coal is burnt, and in rooms in which gas is used, the atmosphere usually contains sulphurous and sulphuric acids in small quantities, and these are liable to act injuriously on certain colours, the former in consequence of its acid and reducing properties, the latter by its acid properties only.

A further desideratum in a good colour is fastness to *rubbing*, by which is meant that the dyed material, when rubbed on a piece of rough white paper or linen, should not colour it. Most colours either do not rub, or can easily be deprived of this property by washing with soap. The defect is most marked, and also very difficult to remove, in the case of several important colours, such as Indigo, dyed Aniline black, and Turkey-red.

Some colours possess the drawback of volatilising from the fibre on which they are dyed at the ordinary temperature of the atmosphere, and are, therefore, totally unsuitable as dyestuffs. A still larger number are partially volatilised in *steaming* or *hot-pressing*, and their employment in printing and in piece goods which are hot-pressed in the process of finishing should, therefore, be generally avoided. Many of the direct cotton colours, especially blues and violets, but also some fast colours, like Alizarin red, are temporarily changed by heat.

Fastness to *stoving*—i.e., to the action of sulphurous acid—is required principally for yarn-dyed wool which is woven into white piece goods (such as blankets), which are subsequently bleached in the piece.

Fastness to *chlorine*, or rather to weak bleaching-powder solution, is required of yarn used, for instance, as headings in towels or other fabrics with coloured stripes which are bleached in the piece.

The *mud* which collects in the streets of towns in wet or moist weather is known to have a destructive action on certain colours in ladies' dress-goods. To what this is actually due does not seem to have been definitely ascertained, but it is generally supposed to be due to limestone or to an alkaline action of the mud caused by the presence of decomposing nitrogenous matter.

Besides these destructive influences, to which dyed goods may be exposed in the ordinary course of things, there are others of minor importance to which the dyer is now and then desired to dye fast shades. The action of light and of washing on dyed colours by far outweigh in importance the action of other agencies; they will, therefore, be considered in the following account.

*Action of Light on Dyed Colours.*—None can have failed to observe that some colours fade more or less rapidly when exposed to light, whereas others undergo no appreciable change. The former are designated *jugitive*, the latter *fast* colours; but between these there are many intermediate degrees. In the



description of the properties of the colouring matters we have classified them in four degrees of fastness—viz., *fast*, *fairly fast*, *moderately fast*, and *not fast*.

As *fast* are to be regarded such colours as Indigo (on wool), Turkey-red, Anthracene brown (on chromium mordant), Aniline black, Sulphide blacks, Indanthrene, Tartrazin, &c., which do not lose appreciably after, say, a month's exposure to direct sunlight in summer.

As *fairly fast*, such colouring matters are classed which, like Methylene blue (on cotton), fustic (on chromium mordant), cochineal (on tin mordant), and the majority of the red, orange, and yellow azo-dyes, lose an appreciable amount of colour during the same time of exposure.

The designation *moderately fast* has been applied to those colours which, like some of the red, orange and yellow azo-dyes on wool, several of the direct cotton colours, some basic colours, &c., are in medium shades strongly affected by two weeks' exposure to direct sunlight.

*Not fast* are those colours which, like the majority of the direct cotton colours and basic colours, show a marked change after a few days' exposure and are more or less bleached after a month's exposure.

It is difficult to give here a more exact classification, as the authors have not had an opportunity of comparing the whole range of natural and artificial colouring matters simultaneously and under exactly the same conditions. Only in this manner can a more accurate comparison be made. That published statements regarding the fastness to light of colouring matters vary considerably is not to be wondered at when we consider how enormously the conditions of exposure may vary with different observers. One observer may expose his patterns in the open air to the joint action of sunlight, wind, rain, and, possibly, frost; another may expose under glass and place the patterns so as to get the largest possible proportion of the direct rays of the sun, or he may perhaps expose in diffused daylight only. Again, the depth of the shade, the climate, the condition of the atmosphere, the time of the year, are all important factors which must necessarily be taken into account if anything like an accurate result is to be arrived at. With the possibility of such varying conditions, it will be easily understood how one observer may obtain a result which leads him to infer that a colour is not fast, whereas another, who may have exposed the same colour for the same length of time, concludes that the colour is fast. It is to be regretted that we have no recognised standard for the testing of colours as to their fastness to light, and much credit would be due to anyone who would take the trouble to work this out. It would undoubtedly be a step in the right direction if, when exposing to direct sunlight under glass, we could agree as to which position the board on which the patterns are fixed should be placed in, and in giving the result, mention the number of hours of direct sunlight (measured by the sun recorder) and of diffused light to which the patterns have been exposed. By a series of experiments the ratio of destructive action of direct sunlight and the average of diffused daylight could possibly be determined, and we should thus be enabled to express the duration of exposure in one term—viz., hours of direct sunlight. If this were done, there would be much less divergency of opinion regarding the fastness to light of colours. For exact measurements, however, it would be necessary to measure the average intensity of the sun's rays during the different seasons of the year and for different climates. (See P. Dosne, *Journ. Soc. Dyers and Col.*, 1901, p. 42).

An important factor in judging of the fastness to light of colours, and one which is not often taken into account, is the condition of the atmosphere. It has been observed that dyed colours exposed in large towns, or in their vicinity, show unmistakable evidence of the presence of acids in the air, while the

air of the country has usually an alkaline reaction. That the presence of ammonia in the atmosphere assists the destructive action of light was pointed out by Berthollet as long ago as 1792, and has been more recently confirmed by experiments recorded in a paper by D. Brownlie.\* In the same paper attention is drawn to the observation that the presence of traces of the vapours of alcohol or pyridine increases the action of light enormously, while solvent naphtha and chloroform slightly retard it.

Direct sunlight acts the most powerfully on dyed colours, diffused daylight is much less destructive. Of artificial lights, the electric arclight resembles sunlight in its action, but it is not so powerful.† In exposing colours dyed on wool under glass to the action of an electric arclight (possessing an illuminating power of 200 gas-flames) at a distance of 1·5 metres, for 1,500 hours, the action was found to be about one-fourth of that of sunlight. Differently-coloured lights act differently on dyed materials.

Herschel first drew attention to the fact that the colouring matters of flowers were most energetically acted upon by the coloured lights complementary to their colours. Dépierre and Clouet‡ studied the effect of white sunlight, electric light, and coloured lights corresponding to the following colours on Chevreul's colour-scale :—

Red	2 R
Orange	4 O
Yellow	G b
Yellowish-green	4 Gr B
Blue	2 B
Violet	1 B

on 76 typical colouring matters (natural and artificial) printed on calico.

The following is a summary of the decolourising action of different lights :—

	Units decolourised.
White sunlight, . . . . .	2256 in 7600.
Blue „ . . . . .	1265 „
Yellow „ . . . . .	1255 „
Green „ . . . . .	968 „
Orange „ . . . . .	856 „
Violet „ . . . . .	713 „
Red „ . . . . .	533 „
White electric light, . . . . .	404 „

The following scheme shows the action of the different-coloured rays on the different colours :—

Strongest action.	Least action.	On material dyed.
Yellow rays.	Red rays.	Red.
Blue „	„	Orange.
Blue „	„	Yellow.
Blue „	„	Green.
Yellow „	„	Blue.
Blue „	„	Violet.

The coloured lights experimented with do not of course represent the corresponding parts of the spectrum, and will all contain more or less white light. The action of differently-coloured lights on dyed fabrics is discussed in a valuable paper by Arthur Dufton.§ Generally speaking, he found from his experiments that a dyed colour is not appreciably affected by a light of the same colour, but is rapidly acted upon by a light possessing the complementary colour to that of the dyed fabric. He concludes that the fading of colours

\* *Journ. Soc. Dyers and Col.*, 1902, p. 295.

† Décaux, *Journ. Soc. Dyers and Col.*, 1885, p. 247.

‡ *Journ. Soc. Dyers and Col.*, 1885, p. 245.

§ *Ibid.*, 1894, p. 90.

under the influence of light is brought about by the absorbed rays; each colour being most powerfully affected by those rays for which it has the strongest absorption.

The subject has also been studied by A. Bolis,\* who maintains that the red, yellow, and green rays of the solar spectrum have little action, while by the blue and violet rays even such a fast colour as Aniline black is strongly affected.

No satisfactory theoretical explanation has hitherto been given of the bleaching action of light. It is probable that light alone cannot bring about such changes. Chevreul exposed several dyed patterns to light in exhausted glass tubes and in tubes filled with indifferent gases, and found that under these circumstances several otherwise very fugitive colours were either unaffected or very much less affected than when exposed under ordinary conditions. Similar observations have since been made by others, working with modern dyestuffs. The yellow colour of raw cotton withstands well the action of light, but after boiling with alkalies, it is soon bleached in direct sunlight. Whether this fact is due to chemical changes brought about by the alkali, or to the removal of the thin covering of cotton wax, has not yet been ascertained, but it is probably due to the latter cause. According to Franc,† dyed colours may be rendered fast to light by impregnating the dyed materials with a solution of linseed oil in naphtha and drying. Many direct cotton colours as well as indigo on cotton are rendered faster to light by a treatment in boiling copper sulphate solution. According to Scheurer ‡ the protective influence of the copper salt is not due, as was at first supposed, to the formation of a lake, but to the fixation of a certain amount of the copper salt in the fibre, which does not permit the chemical rays to pass. It is more probable, however, that the coppering process results in the formation of a copper salt of the dyestuff in or on the fibre.

The theory of the bleaching action of light at present most generally accepted, is that the light causes oxidation and the colours are thereby destroyed. When water evaporates, ozone and peroxide of hydrogen—both powerful oxidising agents—are produced in small quantities, and since, owing to their hygroscopic properties, evaporation or absorption of moisture must always be going on in the textile fibres, with changes in the temperature and the hygrometric condition of the atmosphere, these reactions are regarded as being the principal cause of bleaching. According to D. Brownlie§, the action of light on dyed fabrics represents principally a direct interaction of the colour with the oxygen of the air and with any ozone and hydrogen peroxide present to form colourless substances of unknown composition, and the action is proportional to the moisture present. He endeavours to show that the most favourable atmosphere for the bleaching of colours by sunlight is one which is hot, moist, and alkaline. On the other hand, A. Scheurer maintains that cooled sunlight bleaches more energetically than ordinary sunlight.

According to another theory the bleaching action of light is due to chemical interaction between the dyestuff and the substance of the fibre. Although there is little evidence in favour of this theory, it is evident from the extensive researches on the subject by Ciamician and Silber|| that light alone is capable of effecting drastic changes in organic compounds.

The fastness of a mordant colour to light will depend to some extent on the mode of fixation, but principally on the mordant employed. Thus, fustic dyed on wool on a tin mordant gives a yellow which is not at all fast to light, but with a chromium mordant (bichromate) the yellow obtained with the same colouring matter may be classed as fairly fast. Logwood on chromium mordant

\* *Journ. Soc. Dyers and Col.*, 1909, p. 65.

† *Ibid.*, 1886, p. 94.

‡ *Ibid.*, 1901, pp. 132 and 207; 1904, p. 75, and later numbers of the *Berichte*.

§ *Ibid.*, 1889, p. 44.

|| *Ibid.*, 1902, p. 208.

is not so fast as when dyed on copper mordant. Alizarin blue fixed with zinc gives a fine blue, but the colour thus produced cannot compare in fastness with Alizarin blue fixed on chromium. A great difference is observed with the basic coal-tar colours fixed on Turkey-red oil, on tannic acid, and on tannic acid and tartar emetic respectively. On the oil mordant they are all extremely fugitive, whereas on the tannin and tartar emetic some may be classed as moderately fast. Tannic acid alone holds, as a fixing agent, an intermediate position.

On the other hand, the fastness of a colour will depend in certain cases on the nature of the fibre on which it is dyed. Thus, Indigo is not nearly so fast to light on cotton as on wool, whereas Methylene blue dyed on cotton with tannin and tartar emetic mordant is much faster than on wool.

*Fastness to Washing.*—With certain classes of dyed and printed materials, fastness to washing is of prime importance, whereas with others it is not of much moment. Thus printed calicoes which have to be frequently washed (often with soap and soda), and the colours in figured woollen goods which are milled with soap during the process of manufacture, must necessarily be fast to washing. On the other hand, in such goods as carpets, furniture coverings, and fine silks this fastness is not of great importance.

The behaviour of colours in washing varies enormously. Some, like the ordinary azo-scarlets and oranges fixed on cotton are stripped by water alone. The direct cotton colours dyed on cotton mostly give up a certain amount of colour to boiling water, but only up to a certain point, and no more can be removed unless fresh water be used. Many colours are little affected by boiling water, but are easily affected by soap, especially by such as contains free alkali. Some colours, lastly, like Aniline black, Indigo, and other vat dyes, and most of the Alizarin colours fixed on chromium mordant are fast enough to withstand the action of boiling soap. Since the production of shades fast to washing generally involves a larger number of operations, the use of more costly dyestuffs, and, consequently, greater expense to the dyer, he will, as a rule, employ those dyestuffs and methods which will bring about the desired result in the least time and at the smallest cost, and will only produce fast shades where they are a requirement of the trade, or when specially asked for.

The loss of colour in washing is not the only drawback which the dyer has to guard against, especially in dyed yarns which are used in figured fabrics. Many colours have the disagreeable property, when immersed in water or soap, of colouring other yarns in the piece, especially the whites. Such colours are said to "bleed" or "run," and their use in any fabrics which have to stand washing, other than plain ones, must be carefully avoided.

## METHODS OF TESTING.

Fastness to light is best tested with the colour dyed on a swatch of calico or flannel exposed to light under glass, facing the south if possible. Part of the pattern is covered up with thick cardboard, in order to protect it from the action of the light. At the same time another colour of known fastness and dyed as nearly as possible the same depth of shade on similar material, should be exposed for comparison, or rather in order to get an idea of the relative intensity of the light. The colour should be compared with the unexposed part, say after the first one or two days' exposure, and if it has not faded appreciably it might be left out for a week, a fortnight, or a month. If it has stood a month's exposure in summer without any material alteration, it may be called fast.

Fastness to washing and to bleeding or running should be determined with water alone and with soap. Yarn dyed with the colour is plaited with white

yarn, and the plait boiled in water for ten minutes, wrung, dried, and the dyed yarn compared with the original in order to ascertain whether there has been any loss. It will at once be seen whether the white has remained unaffected, or whether it has been tinged, and, if so, to what extent. Although water only is used, this test is a very severe one, especially in the case of acid colours dyed on wool. In the latter case the bleeding is even more marked than if soap had been used. In a second experiment a plait made as before is worked well in a  $\frac{1}{2}$  per cent. solution of neutral soap (5 grms. to the litre) for 15 minutes at 60°, and the results again compared as above. Some colours behave very differently on wool to what they do on cotton. Thus whereas, for instance, most of the direct cotton colours bleed very much when dyed on cotton, they are quite fast enough on wool to stand milling.

Fastness to acids may be tested in the case of the direct cotton colours by steeping the dyed material in a 5 per cent. solution of acetic acid, and observing whether there is any change in the colour. Cotton warps intended for cross dyeing should not be changed when boiled for 15 minutes in a  $\frac{1}{2}$  per mille solution of sulphuric acid (0.5 gm. in a litre).

Fastness to stoving is generally only required of certain colours on woollen or worsted yarns woven into white pieces to be bleached in the piece. It is tested by working the yarn in very weak soap, wringing, and exposing overnight or for six or eight hours to an atmosphere of sulphurous acid. If in the works, it is best to expose in an ordinary sulphur stove, but if this is not convenient, the yarns may be suspended in a wooden box into which a slow current of sulphurous acid gas is passed from a syphon, or under a bell-jar in which a dish or crucible containing burning sulphur is placed.

Fastness to bleaching may be tested by steeping the cotton yarns after boiling in alkali, for an hour in weak bleaching powder solution (1° to 2° Tw.), washing well in water, then passing through dilute sulphuric acid (1° Tw.), washing again, and drying.

## PART XI.

ANALYSIS AND VALUATION OF MATERIALS USED  
IN DYEING.

In this division we shall treat of the various processes employed for the analysis and valuation of dyes, mordants, and other substances used in the dye-house.

Not very many years ago it was quite the exception to find a dyer troubling himself about any examination of the dyes, &c., which he used; but the importance of attending to this matter is now becoming recognised. The expense incurred by analysis is very small in comparison with the saving thereby often effected. It is, of course, of the greatest importance that care be taken with the analyses, and that the methods employed be capable of giving accurate results. The methods given in the following pages have been carefully selected, and, unless otherwise stated in the text, are known from our own practical experience to be trustworthy and reliable. As will be fully described later on, the majority of dyes should be examined by means of comparative dye-tests; but it is important to bear in mind that, to be of any value, these dye-tests demand as much care and attention as a chemical analysis. Whenever possible, however, a chemical examination is to be preferred.

The methods employed in quantitative chemical analysis may be broadly divided into two classes—viz., *gravimetric* and *volumetric*. In order to determine the amount of a given constituent of a substance by gravimetric analysis, it must either be separated in a pure state, or be converted into a compound of a known and definite composition, purified and weighed. In volumetric analysis the amount of the required body is determined by means of so-called standard solutions—i.e., solutions of a known strength. From the volume of the standard solution required to effect a certain result the weight of the body to be estimated is determined. In a great number of cases no separation whatever is required, the substance being estimated in the presence of several other bodies which have no effect upon the reaction involved. A necessary condition of volumetric analysis is that the end of the operation must be unmistakable to the eye. In the great majority of cases a substance termed an *indicator* is used, which shows, either by a change in colour, or by the formation or disappearance of colour, when the operation is complete. The indicator is sometimes added to the solution under examination, whilst in other cases a drop of the solution is brought from time to time into contact with the indicator outside the liquid. Since volumetric processes are much more rapidly performed than gravimetric, they are, when practicable, almost invariably used in technical analysis. In some cases, however, where no suitable volumetric process is applicable, recourse must be had to gravimetric analysis.

## NORMAL SOLUTIONS.

Some difference of opinion has existed among chemists regarding the significance of normal solutions used in volumetric analysis. Most chemists, however, at the present day are agreed that normal solutions (as described by Sutton) are such that contain in one litre the hydrogen equivalent of the active reagent in grammes. In other words, a litre of a normal solution of any substance is of such a strength that it will exactly neutralise, replace, or oxidise 1 gramme of hydrogen or its equivalent. Normal solutions are, therefore, based upon equivalent weights—not atomic weights. The following table shows a few examples of normal solutions:—

Potassium hydrate, . . . . .	56	grammes	KHO	per litre.
Ammonium „ . . . . .	17	„	NH <sub>3</sub>	„
Sodium carbonate, . . . . .	53	„	Na <sub>2</sub> CO <sub>3</sub>	„
Hydrochloric acid, . . . . .	36.5	„	HCl	„
Sulphuric acid, . . . . .	49	„	H <sub>2</sub> SO <sub>4</sub>	„
Nitric acid, . . . . .	63	„	HNO <sub>3</sub>	„
Sodium chloride, . . . . .	58.5	„	NaCl	„
Silver nitrate, . . . . .	170	„	AgNO <sub>3</sub>	„
Oxalic acid, . . . . .	63	„	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O	„
Potassium permanganate, . . . . .	31.6	„	KMnO <sub>4</sub>	„

A given volume of any of the above *alkaline* solutions will exactly neutralise the same volume of any of the *acid* solutions and *vice versa*. A given volume of the sodium chloride solution will exactly precipitate the silver in the same volume of silver nitrate solution. And again, the potassium permanganate solution will completely oxidise exactly the same volume of oxalic acid. It will be observed that in the case of dibasic acids, one-half of the molecular weight in grammes forms the normal solutions. Also that one-fifth of the molecular weight of potassium permanganate is taken, since one part of this salt is capable of oxidising five parts of hydrogen. The advantages of having solutions made up on this principle are manifold. If, for example, it is required to know the amount of carbonate of soda in a sample of refined soda ash, the number of cubic centimetres of any normal acid required to neutralise 5.3 grammes of the sample expresses the percentage. If 3.1 grms. of the sample were taken, the number of cubic centimetres (c.c.) of any acid required would correspond to the percentage of sodium oxide present. In like manner, by titrating 4.7 grms. of a sample of caustic potash or potassium carbonate with a normal acid, the number of c.c. required to effect neutralisation gives the percentage of potassium oxide (K<sub>2</sub>O) present. By varying the amount of substance weighed out in the proportion of equivalent weights, the use of normal solutions enables the percentage of the body sought to be directly expressed. In many cases it is found in practice more convenient to employ weaker solutions than those above mentioned. For such purposes seminormal, quintinormal, decinormal, and centinormal solutions (indicating solutions one-half, one-fifth, one-tenth, and one-hundredth as strong as normal solutions) are frequently employed, and are usually abbreviated  $\frac{N}{2}$ ,  $\frac{N}{5}$ ,  $\frac{N}{10}$ , and  $\frac{N}{100}$  respectively. In certain technical analyses where a standard solution is used for the determination of one substance only, it may be found more simple and advantageous to employ an empirical standard solution of such a strength that every cubic centimetre shall represent either one decigramme, centigramme, or milligramme of the body to be estimated. For example, supposing a number of analyses of refined alkali (sodium carbonate) are constantly being made for sodium oxide only. A standard acid might be prepared, so that each cubic centimetre neutralised 0.01 gm. Na<sub>2</sub>O, when the number of cubic centimetres required to neutralise 1 gm. of the sample would directly express the percentage.

For fuller particulars regarding the principles of volumetric analysis, works such as Sutton's should be consulted.

**Alkalimetry and Acidimetry.**—These are terms used denoting the methods employed for determining the amount of alkali and acid respectively in various substances. Alkaline bodies are determined by standard solutions of acids and, *vice versa*, acids by standard solutions of alkalies.

**Indicators.**—The exact point of saturation is shown by an indicator. The principal indicators used in alkalimetry and acidimetry are methyl orange, phenolphthalein, lackmoid, cochineal, and litmus. Numerous others have been recommended, but, except perhaps in special cases, they possess no advantages over those enumerated. It must not be supposed that in all cases any one of these indicators is applicable. Although with the stronger mineral acids in conjunction with caustic alkalies all the indicators show the same neutral point—*i.e.*, when the acid and alkali have combined in such proportions as to form a normal salt, there are numerous cases where one indicator shows a neutral reaction with a normal salt and another indicator a neutral reaction with an acid salt of the same base. Sodium sulphite ( $\text{Na}_2\text{SO}_3$ ), for example, is neutral to phenolphthalein and alkaline to methyl orange, whereas sodium bisulphite ( $\text{NaHSO}_3$ ) is neutral to methyl orange and acid to phenolphthalein. There are other cases again where certain indicators are unsuitable on account of a want of precision and sharpness in the end reaction. Phenolphthalein, for example, is unsuitable for titrations with ammonia, and litmus is indefinite with acetic, citric, and other organic acids, as well as in the presence of carbonic acid. The characteristics of indicators have been carefully studied by R. T. Thomson.\*

**Methyl orange.**—This solution may be prepared by dissolving 1 gramme of the colouring matter in a litre of water; 2 or 3 drops of which will be sufficient for each titration. An alkaline solution is of a very pale-yellow colour, but with the slightest excess of acid a pink colouration is developed. It is unaffected by carbonic acid and sulphuretted hydrogen. Carbonates can, therefore, be titrated in the cold.

**Lackmoid** is prepared by the action of sodium nitrite on resorcin. 1 grm. of the colouring matter is dissolved in 100 c.c. of a mixture of equal parts alcohol and water. Alkaline solutions are blue, and acid solutions red; the change being sharp and well defined. Its properties as an indicator are similar to methyl orange. Paper prepared with lackmoid has many advantages over the solution. Lackmoid paper admits of the determination of carbonates and bicarbonates with more precision than the solution. The paper is also of great service in the case of highly-coloured solutions, and in titrating chromates and chromic acid, *bichromates* being exactly neutral to lackmoid.

**Cochineal.**—A solution is prepared by heating 5 grms. of ground cochineal with 500 c.c. of 20 per cent. alcohol, and filtering from the insoluble matter. Its natural colour is orange, which is turned violet by alkalies. It is not appreciably affected by carbonic acid. It is useful in the titrations of alkaline earths and soaps, although it cannot be said to have any distinct advantage over methyl orange.

**Phenolphthalein** is a most useful indicator. One gramme of the substance is dissolved in 100 c.c. of 90 per cent. alcohol. The liquid is colourless in neutral and acid solutions, but the faintest excess of alkali gives an intense red colour. Two or three drops are sufficient for each titration. It is especially serviceable in the estimation of acids with standard solutions of caustic potash or soda. It is not available for ammonia nor for the estimation of carbonates, unless the liquid is well boiled so as to completely expel all carbonic acid. For

\* *Chemical News*, vol. xlvii., pp. 123, 135, 184; vol. xlix., pp. 32, 38, 119; vol. lii., pp. 18, 29.



many weak organic acids it is the only indicator which gives good results. It is also exceedingly useful in the estimation of free caustic alkali in such substances as soap, as well as for free fatty acids in oils, and determination of saponification equivalents of oils, &c., &c.

*Litmus.*—About 10 grms. of solid litmus are ground and treated with 80 per cent. alcohol to remove certain colouring matters not affected by acids and alkalis. The residue is repeatedly treated with cold water, and the solution obtained acidulated with sulphuric acid and boiled. Barium hydrate is now cautiously added to precipitate the sulphuric acid, and the baryta in its turn precipitated by carbonic acid. The liquid is filtered and made up to half a litre. It should be kept in a bottle to which air has free access. Litmus is not serviceable in the presence of free carbonic acid, and it gives no definite end-reaction with most of the organic acids. With mineral acids and caustic alkalis, litmus, like other indicators, is sharp and delicate, but it possesses no advantages over methyl orange. With the two indicators, methyl orange and phenolphthalein, practically all acidimetric and alkalimetric operations can be performed, and most chemists have now discarded litmus altogether in volumetric analysis.

**Preparation of Standard Solutions:—**

#### Normal Sulphuric Acid.

1 litre = 49 grammes  $H_2SO_4$ .

About 30 c.c. of pure concentrated sulphuric acid (preferably distilled) are diluted with four or five times as much water, the mixture allowed to cool, and then made up with more water to a litre. This solution will now require standardising—that is, its strength must be accurately ascertained. For this purpose 1.06 grms. of pure anhydrous sodium carbonate are dissolved in about 100 c.c. of water and a few drops of methyl orange added. The sulphuric acid solution is now run in from a burette until a faint pink colour is produced. The operation is best performed in a white porcelain dish, stirring the liquid with a glass-rod whilst the acid is being run in. If the acid were strictly normal, exactly 20 c.c. would be required, but in all probability it will be found too strong. Suppose 19.5 c.c. of the acid solution were required, it is evident that this amount contains as much sulphuric acid as 20 c.c. of strictly normal acid. Consequently, in order to make the acid of the required strength, all that is necessary is to accurately measure the volume of solution and add water in the proportion of 0.5 c.c. to every 19.5 c.c. Another titration with 1.06 grms. of pure sodium carbonate is now made, when, if care has been duly taken, exactly 20 c.c. of the acid will be required. One standard acid at least should be prepared with the greatest care, leaving no doubt of its accuracy. As sulphuric acid can be very accurately estimated gravimetrically by means of barium chloride, the volumetric determination may be controlled in this way. It is important to bear in mind that the sulphuric acid used should be free from sulphates, otherwise the precipitation method would give too high results. The acid on ignition should leave no appreciable residue, neither should it contain ammonium sulphate. In order to control the strength of normal sulphuric acid gravimetrically, 10 c.c. may be withdrawn by means of an accurate pipette, and diluted with about 150 c.c. of water. A few drops of hydrochloric acid are added, and the liquid heated to the boiling point, when a solution of barium chloride is slowly and carefully added until no further precipitate takes place. The solution is now kept hot for two or three hours on the water bath (the beaker being covered with a clock glass to prevent evaporation), after which time the clear liquid is poured on a filter, and the precipitate treated with boiling water. The barium sulphate is thus washed

two or three times by decantation, when it is wholly transferred to the filter and washed with hot water until free from either barium or chlorine, shown respectively by adding sulphuric acid or silver nitrate to a little of the filtrate. The filter and contents are dried, the precipitate transferred to a weighed crucible, the paper incinerated separately and added to the bulk, and the whole heated at first gently, and then to bright redness for ten minutes, cooled, and weighed. 10 c.c. of normal sulphuric acid treated in this manner should give 1.165 grms. of  $\text{BaSO}_4$ , corresponding to 0.490 grm. of sulphuric acid. From the normal sulphuric acid,  $\frac{N}{2}$ ,  $\frac{N}{5}$ , and  $\frac{N}{10}$  solutions may be prepared by carefully diluting with the requisite amount of distilled water.

Instead of precipitating with barium chloride, F. W. Richardson\* neutralises a given weight of sulphuric acid with barium hydrate solution, evaporates to dryness in a platinum dish, and heats the residue to bright redness.

#### Normal Hydrochloric Acid.

1 litre = 36.5 grammes of HCl.

Hydrochloric acid boiling under the ordinary atmospheric pressure has a constant composition. It contains 20.2 per cent. HCl, and has a specific gravity of 1.10. If 181 grms. or 164.5 c.c. of this acid be diluted to a litre it forms an approximately normal solution, which may be standardised volumetrically exactly in the same manner as sulphuric acid, 1.06 grms. of pure sodium carbonate requiring 20 c.c. of the normal acid as with sulphuric.

#### Normal Caustic Soda.

1 litre = 40 grammes of NaHO.

About 50 grms. of pure caustic soda of commerce (purified by alcohol) are dissolved in a litre of water and the solution (25 c.c. or 50 c.c.) titrated with normal sulphuric acid and methyl orange. The solution will most probably be found too strong. It is carefully diluted with the requisite amount of water (as in the adjustment of sulphuric acid described above), and again titrated when 25 c.c. should be exactly neutralised by 25 c.c. of the normal acid.

The preparation of other standard solutions is given in their respective places when treating of the substances to be analysed.

## ANALYSIS OF ALKALIES AND ACIDS.

**Analysis of Sodium Carbonate.**—Sodium carbonate, in a state of greater or less purity is known in commerce under such names as *soda ash*, *refined alkali*, *crystal carbonate*, *soda crystals*, &c. Soda ash varies greatly in composition; some qualities consisting almost entirely of sodium carbonate, whilst others contain more or less caustic soda, as well as many impurities—sulphides, sulphites, sulphates, iron, calcium, alumina, &c.

In some cases it may only be necessary to determine the amount of total alkali present; in others the caustic soda as well as the carbonate; whilst in others again a more complete analysis may be required.

**Insoluble Matter.**—10 grms. of the sample are dissolved in hot water, filtered, and the residue washed until free from soluble salts. The filter and residue are then dried and ignited in a crucible and weighed.

\* *Journ. Soc. Chem. Ind.*, 1907, p. 78.

**Total Alkali.**—The filtrate and washings are cooled and diluted to a litre; 100 c.c. are withdrawn by means of a pipette, and, with methyl orange as an indicator, titrated with normal sulphuric acid. Each c.c. of acid required corresponds to 0.031 grm.  $\text{Na}_2\text{O}$  or 0.053 grm.  $\text{Na}_2\text{CO}_3$ .

**Caustic Soda.**—250 c.c. of the solution (10 grms. per litre) are put into a 500 c.c. flask, an excess of a perfectly neutral solution of barium chloride added, and the flask filled to the mark with distilled water which has been recently boiled and cooled so as to be free from carbonic acid. The flask is well shaken and then allowed to remain at rest until the precipitated barium carbonate has subsided, when 200 c.c. of the clear supernatant liquor (equal to 100 c.c. of original solution) are withdrawn and titrated with  $\frac{N}{10}$  sulphuric acid. Either methyl orange or phenolphthalein may be used in this case as indicator. Each c.c. of  $\frac{N}{10}$  acid corresponds to 0.0031 grm.  $\text{Na}_2\text{O}$  or 0.004 grm.  $\text{NaHO}$ .

If oxalic acid is used in place of sulphuric or nitric acid, the titration may be carried out in the liquid containing the precipitated barium carbonate, and the time allowed for settling is thus saved.

Caustic soda may also be determined in a *caustic soda ash* by means of strong alcohol, sodium carbonate being insoluble. For this purpose 2 grms. of the sample may be put into a 100 c.c. flask with about 80 c.c. of 96 per cent. alcohol and heated on the water-bath. After cooling, alcohol is added to the mark; the flask is well shaken and allowed to stand for the insoluble carbonate, &c., to subside. 50 c.c. of the clear supernatant liquid are withdrawn and titrated with  $\frac{N}{10}$  acid, as above, using phenolphthalein as indicator. Caustic soda may also be separated and estimated by extracting the sample (about 2 to 5 grms.) with 96 per cent. alcohol in a Soxhlet's apparatus (see *Analysis of Soap*, p. 776). This method is especially to be recommended when it is desired to determine very small quantities of caustic soda in soda ash.

**Sodium Carbonate.**—From the number of c.c. of normal acid required to neutralise 1 grm. of total alkali, the number of c.c. of the same acid required to neutralise the caustic soda in 1 grm. is deducted, and the difference calculated into sodium carbonate.

*Example.*—100 c.c. of a solution (10 grms. per litre) of soda ash (= 1 grm.) neutralised 16 c.c. of normal sulphuric acid.

1 grm. treated as above for caustic soda = 20 c.c.  $\frac{N}{10}$  = 2 c.c. of normal acid.

∴  $0.040 \times 2 \times 100 = 8.00$  per cent.  $\text{NaHO}$ .

16 — 2 = c.c. of normal acid corresponding to carbonate.

∴  $0.053 \times 14 \times 100 = 74.20$  per cent.  $\text{Na}_2\text{CO}_3$ .

**Sodium sulphate** is best determined gravimetrically. 2 to 5 grms. of the sample are dissolved in 100 to 200 c.c. of water and the solution acidulated with hydrochloric acid. The liquid is boiled to expel carbon dioxide, precipitated with a slight excess of barium chloride and treated as described under *Standard Sulphuric Acid* (p. 752). 233 parts of barium sulphate correspond to 142 parts of anhydrous sodium sulphate.

*Example.*—200 c.c. of the solution (= 2 grms.) treated as above yielded 0.1165 grm. barium sulphate.

∴  $\frac{0.1165 \times 100 \times 142}{2 \times 233} = 3.55$  per cent.  $\text{Na}_2\text{SO}_4$ .

**Sodium chloride** may be determined volumetrically by means of silver nitrate, using potassium chromate as an indicator. A decinormal solution of silver nitrate is prepared by dissolving 16.966 grms. of the pure substance in a litre of water. 1 c.c. of this solution = 0.00355 grm. chlorine or 0.00585 grm.

sodium chloride. Before use, this solution should be checked by titrating with it 20 c.c. of a decinormal solution of pure sodium chloride, which should require 20 c.c. for the complete precipitation of the chlorine it contains. Pure sodium chloride is best prepared by dissolving about 50 grms. of common salt in as little water as possible, filtering and passing hydrochloric acid gas (obtained by quickly heating a mixture of common salt and sulphuric acid in a flask) into the solution, which is contained in a beaker. It is best to connect the end of the gas delivery tube to a funnel by means of india-rubber tubing and allow the wide portion of the funnel to dip into the liquid, otherwise the end may become blocked with crystals of salt. The sodium chloride is thus completely precipitated, and after decanting the mother-liquor, which contains magnesium chloride, &c., the pure salt is washed with the least possible amount of water, drained, dried in a porcelain dish, and heated over a flame until all hydrochloric acid is volatilised. The salt is pulverised and bottled whilst quite warm. 5.85 grms. of the pure dry sodium chloride are weighed off, dissolved in water, and made up to 1 litre.

100 c.c. of the soda ash solution (= 1 gm.) are exactly neutralised with  $\frac{N}{10}$  nitric acid (having determined the total alkali, the exact amount of nitric acid can be added direct) in a porcelain basin, a few drops of a solution of potassium chromate are added, and the  $\frac{N}{10}$  silver solution run in from a burette until the liquid acquires a faint orange tint.

*Example.*—100 c.c. of soda ash solution prepared as above and treated as described required 5 c.c.  $\frac{N}{10}$  AgNO<sub>3</sub>.

$$\therefore 5 \times 0.00585 \times 100 = 2.92 \text{ per cent. NaCl.}$$

The operation depends on the fact that when silver nitrate is added to a neutral mixture of a chloride and a chromate, silver chromate, which is of a crimson colour, is not formed until the whole of the chlorine present in the solution has combined to form silver chloride.

Sodium sulphide is indicated by the evolution of sulphuretted hydrogen when the sample is treated with an excess of hydrochloric acid. A more delicate test is sodium nitroprusside. Filter paper saturated with this reagent is dipped into a solution of the sample; if turned blue or violet, a sulphide is present. The amount may be determined by means of a standard solution of ammoniacal silver nitrate. This solution is prepared by dissolving 13.82 grms. of pure silver in dilute nitric acid, adding an excess of ammonia, and making up to a litre; 1 c.c. = 0.005 sodium sulphide. The operation is performed by adding ammonia to 100 c.c. of the soda ash solution (10 grms. per litre), and heating to boiling. The standard solution of silver is then run in until no further precipitate of silver sulphide takes place. The exact point can only be ascertained by filtering a few drops of the liquid, and testing the clear filtrate with a drop of the standard solution. For this and similar operations Beale's filter is very useful.

*Example.*—100 c.c. of soda ash solution required 1.5 c.c. ammoniacal silver nitrate.

$$\therefore 1.5 \times 0.005 \times 100 = 0.75 \text{ per cent. Na}_2\text{S.}$$

Sodium sulphite, together with sodium sulphide, may be determined by means of a decinormal solution of iodine (see p. 783). Add to 100 c.c. of soda ash solution (10 grms. per litre) an excess of acetic acid and a little starch solution. The iodine solution is dropped in until a blue colour is produced. The amount of iodine required by the sulphide (already determined, if present) is calculated (1 c.c. of  $\frac{N}{10}$  iodine = 0.0039 gm. Na<sub>2</sub>S), and deducted from the total amount consumed. The difference represents the sodium sulphite present. 1 c.c. of  $\frac{N}{10}$  iodine = 0.0063 gm. Na<sub>2</sub>SO<sub>3</sub>.

*Example.*—100 c.c. of soda ash solution (10 grms. per litre) treated as above required 1.5 c.c. of ammoniacal silver nitrate for precipitation of the sulphide.

1 c.c. ammoniacal silver nitrate = 0.005 gm. sodium sulphide.

. ∴ 1.5 c.c. = 0.005 × 1.5 = 0.0075 gm.  $\text{Na}_2\text{S}$ .

Another 100 c.c. soda ash solution required 2.1 c.c. of  $\frac{N}{V}$  iodine to produce a blue colour.

1 c.c.  $\frac{N}{V}$  iodine = 0.0039 gm. sodium sulphide.

. ∴ 2.1 c.c.  $\frac{N}{V}$  iodine = 0.0039 × 2.1 = 0.00819 gm. sodium sulphide.

0.00819 - 0.00750 = 0.00069 sodium sulphide to be converted into sodium sulphite.

0.00069 ×  $\frac{63}{39}$  = 0.0011 gm. sodium sulphite.

. ∴ 100 c.c. soda ash contain 0.0011 gm. sodium sulphite.

. ∴ 0.0011 × 100 = 0.11 per cent.  $\text{Na}_2\text{SO}_3$ .

Except in very crude samples of soda ash, the amount of sulphide and sulphite present is usually very small.

**Oxide of Iron and Alumina.**—In several applications of soda ash, iron, if present, even in very small proportions, is a very objectional impurity. If, for example, iron is present in soda ash used for milling woollen cloth previous to dyeing, the fibre absorbs the oxide of the metal, which renders it impossible to obtain subsequently any bright shades with mordant colours. The oxide of iron present is also liable to work on to the cloth irregularly, and when such cloth is dyed, dark stains are produced.

The mixed oxides of iron and aluminium may be estimated by taking about 5 grms. of the sample, dissolving in water, and adding an excess of hydrochloric acid and a little nitric acid. The liquid is boiled and a slight excess of ammonia added. The precipitate is washed at first by decantation, collected on a filter, and thoroughly washed. It is then dried, ignited in a crucible, and weighed. The amount of iron may be determined by dissolving the mixed oxides in hydrochloric acid, or, preferably, by taking a fresh portion (about 5 grms.) of the sample, adding an excess of sulphuric acid, and boiling to expel carbon dioxide and any sulphuretted hydrogen or sulphur dioxide which may be present. The iron is then reduced to the ferrous state by means of pure zinc, as described under iron compounds (*Analysis of Mordants*, p. 792), and then titrated with  $\frac{N}{V}$  potassium permanganate, each c.c. of which corresponds to 0.00112 gm. Fe or 0.00160 gm.  $\text{Fe}_2\text{O}_3$ . If the amount of iron present is very small, it is best determined by colour titration (see *Analysis of Water*, p. 770).

The amount of ferric oxide obtained is then deducted from the *mixed oxides*, the difference giving the *alumina* present, which, however, will probably include a little silica. The silica, if necessary, may be removed and estimated as described under *Analysis of Water*.

Lime may be estimated in the filtrate from the iron oxide and alumina by concentrating and adding a slight excess of ammonium oxalate. Since the amount of lime in any case will only be small, the calcium oxalate after thorough washing may be taken direct with the filter and ignited in a crucible. When the carbon of the filter has been completely burnt, the crucible is cooled, and a little pure sulphuric acid cautiously added. The excess of sulphuric acid is carefully driven off, and the calcium sulphate weighed. 136 parts of  $\text{CaSO}_4$  = 56 parts of CaO. Lime may be more quickly determined by transferring the well-washed precipitate of calcium oxalate to a beaker, adding hot dilute sulphuric acid, and titrating with standard permanganate (see *Analysis of Water*, p. 771).

**Water.**—Since the value of soda ash and other forms of sodium carbonate is determined by direct analysis, the estimation of water is not of much importance.

In the case of a complete analysis, however, it should not be omitted. About 2 grms. of the sample are gently ignited to low redness in a crucible for 20 to 30 minutes. With a carbonated alkali the loss in weight may be directly calculated as water; but if caustic soda be present, it will, under ordinary conditions, absorb carbon dioxide with formation of carbonate. A dry soda ash containing caustic soda may be found to be heavier after ignition than before. If the operation is performed in a shallow platinum capsule, the caustic soda present will usually, in the course of an hour or so, become completely converted into carbonate. The conversion into carbonate may be ensured by addition of ammonium carbonate. The amount of  $\text{CO}_2$  thus absorbed is calculated from the caustic soda present, and added to the loss in weight sustained on heating.

**Analysis of Caustic Soda.**—*Sodium Hydrate.*—The methods given under sodium carbonate are used also for caustic soda, the chief difference being that, whereas soda ash, &c., consist essentially of sodium carbonate with (possibly) small quantities of sodium hydrate, commercial caustic soda consists essentially of sodium hydrate with (possibly) small quantities of sodium carbonate.

Small quantities of carbonate in caustic soda may be conveniently estimated in the following manner:—A weighed amount of the sample is dissolved in about 200 c.c. of cold water (free from  $\text{CO}_2$ ), and a few drops of phenolphthalein added. Normal sulphuric acid is slowly and carefully added until the red colour is just discharged. At this point the caustic soda is completely neutralised, and the carbonate converted into bicarbonate. A few drops of methyl orange are now added to the solution, and the addition of normal acid continued until an orange colour appears. The number of c.c. of acid required after adding methyl orange multiplied by 2 represents the amount of sodium carbonate present. Deducting that number from the total amount of acid consumed, the difference represents the sodium hydrate.

*Example.*—10 grms. of caustic soda were dissolved in 500 c.c. of water. 50 c.c. (= 1 gm.) were taken, diluted with cold (recently boiled) distilled water, and with phenolphthalein titrated with normal acid, as above described. 18 c.c. were required. After adding methyl-orange, 0.3 c.c. of acid was required.

1 c.c. of normal acid = 0.040 gm.  $\text{NaHO}$ , or 0.053 gm.  $\text{Na}_2\text{CO}_3$ .

∴  $0.053 \times 1.6 \times 100 = 8.48$  per cent.  $\text{Na}_2\text{CO}_3$ .

$0.040 \times 17.2 \times 100 = 68.80$  „  $\text{NaHO}$ .

In place of the methyl orange and phenolphthalein, Lunge\* has recommended the use of phenacetolin for estimating carbonates in presence of caustic alkalies. A solution of the indicator of suitable strength is prepared by dissolving 2 grms. in a litre of alcohol. This indicator is of a yellow colour in presence of caustic soda and potash and free mineral acids, but red in presence of carbonates and bicarbonates. A few drops of the indicator are added to the solution to be tested, and normal acid added until the liquid acquires a rose-red tint. The volume of acid consumed corresponds to the amount of caustic alkali present. The addition of acid is now continued, the liquid becoming of a deeper red until suddenly it again becomes yellow. The second volume of acid added corresponds to the amount of sodium carbonate present.

**Analysis of Potassium Carbonate.**—*Pearl Ash—Potash.*

**Analysis of Caustic Potash.**—*Potassium Hydrate.*

The analysis of potassium carbonate and caustic potash does not differ essentially from that of the corresponding sodium compounds—

1 c.c. of normal acid = 0.069 gm.  $\text{K}_2\text{CO}_3$   
 = 0.056 „  $\text{KHO}$   
 = 0.047 „  $\text{K}_2\text{O}$ .

\* *Journ. Soc. Chem. Ind.*, 1882, p. 56.

**Estimation of Potash by Platinum Chloride.**—Since potash salts frequently contain considerable quantities of soda salts, either as natural impurities or adulterations, it is often necessary to estimate the amount of real potash present. The alkalimetric process, of course, would include soda, if present. The best method for estimating potassium in presence of sodium salts, although often considered too tedious and expensive for technical purposes, is undoubtedly by precipitation with platinum chloride. 5 grms. of the sample are dissolved in 500 c.c. of water. If any insoluble matter be present it can be allowed to subside, and 25 c.c. of the clear solution drawn off and introduced into a porcelain dish. A slight excess of hydrochloric acid is added, the dish being covered with a clock glass to prevent loss from effervescence. The clock glass is removed, taking care to wash the under side into the dish, an excess of platinum chloride added, and the solution evaporated *nearly* to dryness on a water bath. The solution should remain highly-coloured yellow during the whole of the evaporation. If it becomes colourless, or nearly so, more platinum chloride solution must be added. The dish is allowed to cool (the residue should be still moist), and a mixture of alcohol and ether added in order to dissolve the excess of platinum chloride and sodium salts present. After 10 or 15 minutes the liquid is decanted through a small filter, and the operation repeated four or five times, until, in fact, the filtrate is not only colourless, but also leaves no more than the slightest stain when a drop or two are evaporated on a watch-glass. The bulk of the precipitate will be left in the basin, but a small quantity will also be on the filter. The precipitate is transferred to a small weighed platinum or porcelain basin, and the small portion on the filter also washed in by means of hot water. The liquid is evaporated to dryness and dried at 100° C. in the water oven and weighed.

485 parts of the precipitate ( $K_2PtCl_6$ ) correspond to 138 parts of  $K_2CO_3$ .

If the substance to be analysed contains more than traces of sulphates, the sulphuric acid should be removed by barium chloride, otherwise the potassium platinum chloride is liable to be contaminated with sodium sulphate. This, however, may be prevented without practically affecting the accuracy of the results by having an excess of hydrochloric acid present, and allowing about half a cubic centimetre of liquid to remain in the dish before adding alcohol and ether. During the whole of the process, care should be taken to prevent access of vapours of ammonia, since ammonia also gives a double salt with platinum chloride, possessing similar properties to the potassium compound.

**Estimation of Potash by Tartaric Acid.**—2 grms. of the sample are washed into a small flask with about 25 c.c. of water, and neutralised by tartaric acid. 50 c.c. of a saturated solution of sodium bitartrate are added to the flask, and well shaken at intervals during the course of an hour. The precipitated potassium bitartrate is then collected on a small filter and washed with a cold saturated solution of potassium bitartrate. The filter and contents are put back into the flask, which may contain a little of the precipitate, hot water added, and the solution, with phenolphthalein as an indicator, titrated with normal caustic soda.

1 c.c. of normal soda = 0.069 grm.  $K_2CO_3$  or 0.056 grm. KHO.

**Indirect estimation of Potash and Soda.**—From 0.5 to 1 grm. of the sample is dissolved in water and a slight excess of hydrochloric acid. The solution is heated to the boiling point and, if any sulphates are present, barium chloride added. The barium sulphate is removed by filtration, and the excess of barium in solution precipitated by ammonium carbonate and ammonia. The filtrate from the barium carbonate precipitate is evaporated to dryness in a platinum dish, and the residue ignited to expel ammonium compounds. After cooling, the ignited residue is treated with hot water, and the solution filtered from any

insoluble matter. The clear filtrate and washings, with addition of a little hydrochloric acid, are now evaporated to dryness in a weighed platinum dish, and the residue heated to about 180° C. in an air-bath, cooled, and weighed. This gives the mixed potassium and sodium chlorides present in the sample, and by estimating the combined chlorine, the amount of potassium and sodium chloride respectively can be calculated. The chlorides are dissolved in water and diluted to 500 c.c.; 50 c.c. are withdrawn and titrated with  $\frac{N}{10}$  silver nitrate, as given under *Analysis of Sodium Carbonate* (p. 754). Each c.c. = 0.00355 grm. Cl. The amount of potassium is found by multiplying the difference between the mixed chlorides and chlorine by 1.54, subtracting the chlorine and dividing by 0.63.

**Analysis of Ammonia.**—*Ammonium Hydrate.*—Two qualities are known in commerce—viz., *gas liquor ammonia* and *sulphate ammonia*. The strongest *liquor ammonia* of commerce has a specific gravity of 0.880 and contains about 30 per cent. of  $\text{NH}_3$ . A close approximation of the strength of a solution of ammonia may be ascertained by a careful determination of its density. For this purpose a specific gravity flask marked on the neck to hold 25 grms. of distilled water may be conveniently used. The dry flask is tared, carefully filled with the ammonia and again weighed. The weight of the sample thus obtained divided by 25 gives its specific gravity (water = 1), and on reference to tables the percentage of  $\text{NH}_3$  is ascertained. The flask should be filled with distilled water and weighed to see that it really does hold exactly 25 grms. The specific gravity may also be taken by means of a delicate hydrometer.

The table on p. 215 shows the amount of  $\text{NH}_3$  in solution of various densities according to Lunge and Wiernik.

**Estimation of Free Ammonia by Titration.**—The 25 c.c. of ammonia used in taking the density, of which the weight is therefore known, may be diluted with water to 500 c.c. Of this solution 50 c.c. are withdrawn and, with methyl orange as an indicator, titrated with normal sulphuric acid.

$$1 \text{ c.c. of normal acid} = 0.017 \text{ grm. NH}_3.$$

*Example.*—25 c.c. of a sample of ammonia weighed 22.888 grms. Specific gravity, therefore, =  $\frac{22.888}{25} = 0.9155$ . The 25 c.c. were diluted to 500 c.c., and 50 c.c. of this solution required 31.8 c.c. of normal sulphuric acid.

$$\therefore \frac{0.017 \times 31.8 \times 10 \times 100}{25 \cdot 888} = 23.60 \text{ per cent. NH}_3.$$

*Gas liquor ammonia* may contain sulphides and tarry matter, which for some purposes are objectionable. Sulphides may be detected by the violet colour imparted to paper saturated with a solution of sodium nitroprusside. The presence of tarry matter is indicated by the smell which is gradually developed when a sample of ammonia is allowed to evaporate spontaneously. Commercial samples of ammonia, when neutralised by nitric acid, frequently develop a rose-red colour and a peculiar odour, due to the presence of minute quantities of certain organic bases.

**Estimation of Combined Ammonia.**—The titration of ammoniacal solutions with standard acid as detailed above only shows the amount of free ammonia present. If the ammonia is in combination with an acid, as in ammonium sulphate, the total ammonia may be determined by distilling a weighed amount of the substance in solution with lime, baryta, magnesia, potash, or soda, preferably the last mentioned substance. The evolved ammonia is collected in a known volume of standard acid and titrated back with standard alkali, or absorbed in an excess of hydrochloric acid and the ammonium chloride thus formed estimated by precipitation with platinum tetrachloride.



The total ammonia found by distillation less the amount found by titration gives the quantity which is present in combination with acids. 1 grm. of the ammonium salt is weighed and transferred to a flask of about 200 c.c. capacity, together with 25 c.c. of water. The flask must have been previously fitted with a rubber cork having two openings, through one of which passes a tapped funnel holding a strong solution (10 per cent.) of caustic soda. A glass tube about 30 inches long is inserted in the other opening and inclined upwards at an angle of about 30° in order to prevent any alkali being carried over mechanically with the ammonia. The other end of the tube is bent downwards and passed through a cork into a flask of about 500 c.c. capacity containing 40 c.c. of normal sulphuric acid. The outlet of this receiving flask is fitted with a short wide tube containing glass wool or glass beads through which the standard acid has been poured. Both ends of the distilling tube should be cut off at a sharp angle, and the one in the receiver must reach nearly to the surface of the standard acid. During the distillation the receiver must be kept cool by being placed in a vessel of cold water. Heat is applied to the small flask as soon as the caustic soda solution has been run in. The liquid should be boiled for about thirty minutes. The small tube containing the glass-wool saturated with sulphuric acid is washed well with distilled water into the flask, and the residual acid determined by normal caustic soda, using methyl orange as indicator.

*Example.*—1 grm. of ammonium sulphate was distilled, as above described, into 40 c.c. of normal sulphuric acid. The acid remaining neutralised 25 c.c. of normal soda; therefore, 15 c.c. of acid were neutralised by the ammonia.

$$1 \text{ c.c. of acid} = 0.017 \text{ grm. NH}_3.$$

$$\therefore 0.017 \times 15 \times 100 = 25.50 \text{ per cent. NH}_3.$$

If it is desired to estimate the ammonia gravimetrically, hydrochloric is used in place of sulphuric acid. After the distillation, the acid solution of ammonium chloride is poured into a porcelain dish, platinum chloride solution added, and the whole evaporated nearly to dryness on the water-bath. The double chloride of ammonium and platinum thus formed is treated in exactly the same manner as the corresponding potassium compound described under potash salts (p. 758). 442.5 parts of  $(\text{NH}_4)_2\text{PtCl}_6$  correspond to 34 parts of  $\text{NH}_3$ .

*Example.*—0.5 grm. ammonium sulphate was distilled with soda, as explained above, and the acid distillate on treating with platinum chloride yielded 1.6785 grm.  $(\text{NH}_4)_2\text{PtCl}_6$

$$\frac{1.6785 \times 34 \times 100}{442.5 \times 5} = 25.80 \text{ per cent. NH}_3.$$

**Analysis of Sulphuric Acid.**—*Oil of Vitriol.*—By a careful determination of its specific gravity, the strength of a sample of sulphuric acid may be approximately ascertained. The exact temperature at which the density is taken must be noted and, if necessary, corrections made, otherwise the results will be incorrect. A difference of 2° C. in the temperature may, if neglected, cause an error of 3 per cent. of sulphuric acid calculated from tables.

The tables given on pp. 164 and 165 show the strength of sulphuric acid of different densities.

**Titration.**—25 c.c. of the sample accurately weighed are diluted with water to a litre. 25 c.c. are withdrawn and titrated with normal caustic soda and methyl orange. 1 c.c. = 0.049 grm.  $\text{H}_2\text{SO}_4$ . The strength of the acid may also be ascertained by running the dilute solution from a burette into a solution of pure sodium carbonate. If 1.082 grms. of sodium carbonate is taken, the number of c.c. of acid required to neutralise it contains exactly 1 grm. of  $\text{H}_2\text{SO}_4$ .

*Example.*—25 c.c. of sulphuric acid weighing 46 grms. were diluted to a litre.

1.082  $\text{Na}_2\text{CO}_3$  neutralised 22.5 c.c. acid.

22.5 c.c. . . . contains 1 grm.  $\text{H}_2\text{SO}_4$ .

1,000 c.c. . . . „ 44.44 grms.  $\text{H}_2\text{SO}_4$ .

$$\therefore \frac{44.44 \times 100}{46} = 96.60 \text{ per cent. } \text{H}_2\text{SO}_4.$$

Sulphuric acid of commerce is liable to contain numerous impurities, chief amongst which are sulphates of lead, iron, and soda, arsenious acid, and nitrogen acids. Arsenic is very often present in very considerable quantities in acid made from pyrites.

Sulphate of lead is indicated by the formation of a white precipitate on dilution with water. It may be estimated by taking about 25 c.c. of the sample and adding 25 c.c. of water and 50 c.c. of alcohol. The liquid is filtered and the precipitate washed thoroughly with alcohol. The lead sulphate is dried, ignited in a porcelain crucible, and weighed. This determination, however, is not often necessary; it usually suffices to ignite about 10 grms. of the acid in a crucible and weigh the residue. The amount obtained, as a rule very small, of course includes sodium sulphate, if present.

Iron may be determined by igniting 10 to 20 grms. and treating the residue as given under *Analysis of Water* (p. 770).

The estimation of iron direct by reduction with zinc and subsequent titration with potassium permanganate cannot be recommended, since arsenic, if present, would seriously interfere with the reaction.

**Nitrogen Acids.**—Nitrogen compounds in sulphuric acid are especially mischievous in acid used for dissolving indigo, since a portion of the colouring matter is thereby destroyed, and the resulting extract is not so bright. They may be detected by carefully pouring a solution of ferrous sulphate into a test-tube containing the acid, the formation of a brownish-purple ring where the two liquids meet indicating the presence of oxides of nitrogen. A more delicate method, recommended by Thorp Whitaker,\* is the following:—25 to 50 c.c. of the acid are diluted with half the volume of water, and a drop of a 1 per cent. alcoholic solution of diphenylamine added. The liquid, on stirring with a glass rod, becomes coloured blue in the presence of nitrogen acids. The depth of the colouration is in proportion to the amount present. On standing, the colour gradually disappears.

According to Lunge, this test fails, however, in the presence of selenium (which can be recognised by adding to the acid a strong solution of ferrous sulphate, when a brownish-red precipitate will make its appearance, which cannot be confounded with the colour produced by the test for NO mentioned above). If selenium be present the nitrogen acids are detected by the addition of brucine sulphate solution to the diluted acid, a red colour demonstrating their presence.

Arsenic, if present in considerable quantities, is readily detected by diluting about 25 c.c. with 150 c.c. of water, and passing a current of sulphuretted hydrogen through the liquid. A yellow precipitate indicates arsenic, which may further be confirmed by treating the precipitate with a strong solution of ammonium carbonate, in which reagent arsenious sulphide is soluble.

If the yellow precipitate from a given weight of acid (about 50 grms.) be collected on a weighed filter paper, washed thoroughly, dried at  $100^\circ \text{C}$ ., and weighed, the amount of arsenic present may be ascertained.

246 parts of the precipitate  $\text{As}_2\text{S}_3 = 198$  parts of  $\text{As}_2\text{O}_3$ .

\* *Journ. Soc. Dyers and Col.*, 1885, p. 91.

Blattner and Brasseur\* estimate arsenic in sulphuric acid (also in hydrochloric acid) by converting it into the tri-iodide which is nearly insoluble in strong acids. 25 c.c. of the acid, which should be approximately of 1.45 sp. gr., are mixed with 25 c.c. of pure hydrochloric acid and 5 c.c. of a 30 per cent. solution of potassium iodide. The precipitate of arsenic tri-iodide is filtered off through glass wool, washed with pure hydrochloric acid containing 10 per cent. of the potassium iodide solution, and dissolved in water. Sodium bicarbonate is added and the solution titrated with  $\frac{N}{10}$  iodine, each c.c. of which equals 0.00375 grm. of arsenic.

Small quantities of arsenic are best detected and estimated by Marsh's test as given under *Textile Fabrics*.

**Analysis of Sodium Sulphate.**—Sodium sulphate is met with in the market as *salt-cake* and as *Glaubersalt*, or crystallised sodium sulphate. The latter (made by crystallising from salt-cake) is used in very large quantities in numerous dyeing operations. It is rarely necessary to make an examination of this substance unless it be to test for iron and free sulphuric acid when used for dyeing unions. Salt-cake usually contains about 95 per cent. of anhydrous sodium sulphate. The impurities are aluminium, calcium, and ferric sulphates, free sulphuric acid (as bisulphate), sodium chloride, insoluble matter, and water. The amount of sodium sulphate may either be estimated direct or ascertained by determining the amount of total impurities. These impurities may be estimated by the methods given under sodium carbonate (p. 753). For the direct estimation, Grossmann's process,† described in Sutton's *Volumetric Analysis*, is to be recommended. Briefly, about 4 grms. of the salt are dissolved in water, and an excess of barium hydrate added, which precipitates the sulphuric acid as well as oxide of iron and alumina. A stream of carbon dioxide is passed through an aliquot part of the filtered solution, and the liquid boiled, by which means the excess of baryta and any lime are removed. The liquid is again filtered, and an aliquot part titrated with standard sulphuric acid. 1 c.c. of normal acid = 0.071 grm.  $\text{Na}_2\text{SO}_4$ . For details as to the necessary corrections see the works mentioned.

**Analysis of Sodium Sulphide.**—Sodium sulphide is used in great quantities in the dyeing of sulphur colours. It comes into the market in two forms; crystalline, containing 9 molecules of water, and in the more or less anhydrous state. It may be estimated by means of a decinormal iodine solution with starch as an indicator. 10 grms. of the sample are dissolved in a litre of water, and this solution run into 25 c.c.  $\frac{N}{10}$  iodine solution diluted with 100 c.c. water, containing a little acetic acid. When nearly colourless a little starch solution is added and the titration continued until the blue colour is discharged. 1 c.c.  $\frac{N}{10}$  iodine = 0.012 grm.  $\text{Na}_2\text{S}$ , 9  $\text{H}_2\text{O}$ .

**Analysis of Hydrochloric Acid** (*Muriatic Acid, Spirits of Salt*).—The crude acid, obtained in enormous quantities as a secondary product in the manufacture of soda ash, is usually of a yellow colour, due to the presence of organic matter and iron. Other impurities which may be present are sulphuric acid, common salt, and arsenic. The strength of the pure acid may be conveniently ascertained by a determination of its density. The usual impurities, even in the crude acid, have little effect upon the density, although, of course, it is possible for the acid to be adulterated with common salt. The strongest solution of hydrochloric acid has a density of 1.21, and contains 43 per cent. HCl. The usual strength of commercial acid is 1.16 specific gravity, which contains 32 per cent. HCl. The table on p. 167 shows the percentage of HCl in solutions of various densities.

\* *Chem. Zeit.*, 1904, p. 211; *Journ. Soc. Chem. Ind.*, 1904, p. 338.

† *Chem. News*, vol. xli., 1880, p. 114.

**Titration of Hydrochloric Acid** is performed in exactly the same manner as that of sulphuric acid. 50 c.c. of the sample are weighed and diluted to a litre; 100 c.c. of this solution titrated with normal caustic soda. 1 c.c. = 0.0365 grm. HCl.

If sulphuric acid be present it will be necessary to deduct the acidity due to that acid (determined gravimetrically) from the total acidity, after making allowance for any sodium sulphate present.

*Sodium chloride* is determined by evaporating a weighed portion of the acid to dryness, igniting gently, and testing with  $\frac{N}{10}$  silver nitrate.

*Sodium sulphate* may be estimated by evaporating and igniting as in the preceding test, dissolving in water, filtering off insoluble matter, and evaporating to dryness. The residue, which consists of sodium chloride and sodium sulphate, is weighed. After deducting the amount of sodium chloride found as above, the remainder is reckoned as sodium sulphate. The residue should be tested for lime, which may be present in small quantities.

*Arsenic* and *iron* may be determined as in sulphuric acid.

**Analysis of Nitric Acid.**—Two qualities of ordinary nitric acid are known in the trade—viz., *single aqua fortis*, having a density of 1.165, and containing 27 per cent. of  $\text{HNO}_3$ ; and *double aqua fortis*, having a density of 1.325, and containing about 51 per cent. of  $\text{HNO}_3$ .

The amount of  $\text{HNO}_3$  in solutions of nitric acid of various densities is given in the table on p. 169.

**Titration of Nitric Acid.**—50 c.c. of the sample are weighed and diluted to a litre, and 100 c.c. of this solution taken for titration. 1 c.c. of normal caustic soda = 0.063 grm.  $\text{HNO}_3$ .

The usual impurities in commercial nitric acid are *sulphuric acid*, *hydrochloric acid*, and *sodium nitrate*. These may be readily detected and estimated by processes already described.

**Analysis of Sodium Nitrite.**—This salt is used in the manufacture of azo-colours and some other dyestuffs, and in the dyehouse for the production of azo-colours on the fibre. Sodium nitrite may be conveniently determined by potassium permanganate solution. 1 grm. of the sample is dissolved in about 300 c.c. of cold water; to this liquid  $\frac{N}{10}$  permanganate is added drop by drop until it has a permanent red colour, then a few drops of dilute sulphuric acid, and immediately afterwards a known excess of the permanganate. The liquid, which should now be of a dark red colour, is strongly acidified with sulphuric acid, heated to boiling, and the excess of permanganate determined by means of  $\frac{N}{10}$  oxalic acid. 1 c.c.  $\frac{N}{10}$  permanganate = 0.00345 grm.  $\text{NaNO}_2$ .

**Analysis of Acetic Acid.**—Acetic acid for technical purposes is obtained largely by the distillation of wood. The crude acid known as *pyroligneous acid* contains, in addition to acetic, a number of other acids as well as acetone, other ketones, wood oils, &c. By neutralising with lime and distilling the purified acetate of lime with a mineral acid, a purer acetic acid is obtained. Pure acetic acid has a density of 1.055, but a solution containing 43 per cent. of acetic acid also possesses the same density. On account of this anomaly a direct determination of the specific gravity cannot be utilised for ascertaining the strength of solutions of even pure acetic acid except in those cases where the density is lower than 1.055. By diluting the liquid with water, however, and taking the density again, one may ascertain whether the sample contains more or less than 77 per cent. of acid (see p. 170). With the crude acid, the specific gravity is no criterion whatever.

The table on p. 170 shows the percentage of acetic acid in solutions of various densities.

**Titration.**—In estimating acetic acid, *phenolphthalein* should be used as indicator. The end reaction is sharp, and even with highly-coloured

liquids, if diluted, the termination is usually unmistakable. Litmus, methyl orange, and other indicators are not suitable for acetic acid. 25 c.c. of the sample are weighed and diluted to 500 c.c.; 100 c.c. are withdrawn and, with addition of a few drops of phenolphthalein solution, titrated with normal caustic soda. 1 c.c. = 0.060  $C_2H_4O_2$ . In cases where the acid is of a very deep brown colour the following process recommended by Mohr may be used. About 5 grms. of the sample are treated with a known weight of pure calcium carbonate in excess. The liquid is boiled and filtered; the residue washed with hot water, and the undissolved calcium carbonate dissolved in a known excess of standard nitric acid and titrated back with caustic soda.

*Example.*—5.2 grms. were treated with 2 grms. of  $CaCO_3$ , as above. To the residual  $CaCO_3$ , 20 c.c. of normal nitric acid were added, and it was found that 6 c.c. of normal caustic soda were required to neutralise the liquid. Consequently, residual calcium carbonate neutralised 14 c.c. of normal nitric acid = 0.7 gm.  $CaCO_3$ . The acetic acid in 5.2 grms. of sample, therefore, neutralised 1.3 grms. of  $CaCO_3$  = 1.56 grms.  $C_2H_4O_2$  (100  $CaCO_3$  = 120  $C_2H_4O_2$ ).

$$\therefore \frac{1.56 \times 100}{5.2} = 30 \text{ per cent. of } C_2H_4O_2.$$

*Commercial acetic acid* is liable to contain as impurities and adulterations sulphuric acid and sulphates; hydrochloric acid and chlorides; iron, lead, and calcium.

*Sulphuric acid*, free and combined, is detected and estimated by precipitation with barium chloride;

*Hydrochloric acid*, free and combined, by silver nitrate;

*Calcium salts*, by addition of ammonium oxalate;

*Iron and Lead* as in sulphuric acid.

*Total solid matter* may be determined by evaporating 20 c.c. to dryness and drying in the air bath at 110°.

*Empyreumatic and other organic bodies*, if present in large quantities, may be at once detected by the colour and smell. Smaller amounts may be detected by neutralising with sodium carbonate, and gently warming the solution. Acetic acid containing these organic bodies darkens in colour when heated with concentrated sulphuric acid. An approximate estimation of the empyreumatic bodies present may be made by diluting 5 or 10 c.c. with 500 c.c. water, adding dilute sulphuric acid, and titrating with decinormal permanganate until the pink colour remains for about a minute.

*Free mineral acids* may be detected by moistening a strip of white calico with the acid and drying at 90° to 100°. If hydrochloric or sulphuric acid be present the fibre is "tendered," disintegrated, or even charred. *Free sulphuric acid* may be detected and estimated by evaporating 10 to 50 c.c. to a syrup, and, when cold, adding strong alcohol. Free sulphuric acid remains in solution, whereas sulphates are precipitated. The liquid is filtered and diluted with water, the alcohol boiled off and barium chloride added. The barium sulphate is then treated in exactly the same manner as previously described.

*Estimation of Acetic Acid in Calcium Acetate and other Acetates.*—The amount of acetic acid present is determined by distillation with phosphoric acid, as recommended by Stillwell and Gladding,\* and described in *Allen's Commercial Organic Analysis*, vol. i., p. 398. A retort of 100 c.c. capacity, the tube of which should have been previously bent downward about 4 inches from the end, is employed. The extremity of the retort is connected with a small Liebig's condenser, the inner tube of which at its lower end passes downward into a flask containing water.

\* See also A. G. Stillwell, *Journ. Soc. Chem. Ind.*, 1904, p. 305, and W. M. Grosvenor, *ibid.*, *Journ. Soc. Chem. Ind.*, 1904, p. 530.

The receiver consists of a wide-mouthed flask of 1 litre capacity, fitted with a rubber stopper having two holes, through the smaller of which passes the narrow end of a small tube (such as is used for drying purposes) filled with glass beads. The water should be poured down this tube, the retort tubulus being meanwhile left open. The receiving flask should be placed in a vessel of cold water and kept cool during the distillation.

One gram. of the sample is worked through a wide short-necked funnel into the retort with 15 c.c. of water. The retort is fitted with a tapped funnel, through which is poured a solution of 5 grms. of glacial phosphoric acid in 10 c.c. of water. During the operation the neck of the retort is inclined slightly upwards to prevent any liquid being carried over mechanically.

The retort, which is placed on wire gauze, is gently heated, and the liquid distilled until it is reduced to a volume of not more than 10 c.c., when 25 c.c. of water are introduced through the funnel, and the distillation continued until the volume of the liquid is again reduced to 10 c.c. The addition of water and distillation to small bulk are repeated three more times, when the whole of the acetic acid will have passed over. The distillate, after rinsing the condenser into the receiver, is titrated with  $\frac{N}{5}$  caustic soda and phenolphthalein. Each c.c. corresponds to 0.012 gm. of  $C_2H_4O_2$  or to 0.0158 gm.  $Ca(C_2H_3O_2)_2$ . The phosphoric acid used must be free from nitric acid. If the sample or phosphoric acid contain chlorides, a little silver sulphate must be added to the contents of the retort to prevent hydrochloric acid distilling over.

*Example.*—1 gram. of a sample distilled as above described required 54 c.c.  $\frac{N}{5}$  NaOH.

$$\therefore 0.012 \times 54 \times 100 = 64.80 \text{ per cent. acetic acid ; or,}$$

$$0.0158 \times 54 \times 100 = 85.32 \text{ per cent. calcium acetate.}$$

**Analysis of Formic Acid.**—This acid is now used in the dyehouse to a considerable extent in place of acetic, sulphuric, and other acids. Having no action on cotton it replaces sulphuric acid with advantage in the dyeing of union goods. When used in chroming it causes a complete exhaustion of the chrome bath. In the absence of other acids, formic acid may be determined by a standard solution of caustic soda, using phenolphthalein as indicator. Each c.c. of normal alkali corresponds to 0.046 gm.  $H_2CO_2$ . In the presence of acetic acid or other easily oxidisable organic substances, A. Leys\* makes use of mercuric acetate for the determination of formic acid. One molecule of mercuric acetate is reduced to mercurous acetate by one molecule of formic acid. In the first place, the total acidity is determined by means of caustic soda and phenolphthalein. If the solution contain only a small quantity of formic acid and a large quantity of acetic acid it is diluted until only about 20 to 30 per cent. of acid is present ; if, however, the proportion of formic acid amount to 1 in 20 of acetic acid or more, it is diluted so as to contain only about 2 per cent. of acid. To 10 c.c. of the solution 20 to 30 c.c. of a 20 per cent. solution of mercuric acetate are then added, the mixture made up to 100 c.c., and boiled for seven or eight minutes. After cooling and standing overnight, the crystalline precipitate is filtered off through glass wool, drained, and washed four or five times with alcohol containing 2 per cent. by volume of glacial acetic acid, then two or three times with alcohol alone, and finally with anhydrous ether. After drying, preferably *in vacuo*, the mass is dissolved in nitric acid, and diluted to a suitable given volume. 10 c.c. are diluted largely with water and precipitated by a slight excess of sodium chloride. The mercurous chloride is filtered, washed, dried at  $100^\circ$ , and weighed. The weight of mercurous chloride, multiplied by 0.0976, gives the amount of formic acid in the aliquot part of solution taken.

\* *Journ. Soc. Chem. Ind.*, 1898, p. 957.

F. Sparre\* also determines formic acid in the presence of acetic acid by its reducing action upon mercuric salts, and proceeds as follows:—Five grms. of sodium acetate, 200 c.c. of a 4.5 per cent. solution of mercuric chloride are brought together in a flask with 25 c.c. of a 1 per cent. solution of the liquid under examination. After heating for 1 to 1½ hours in a water-bath, the volume of the liquid is made up to 500 c.c. The amount of formic acid present is estimated by finding how many c.c. of the filtered liquid are necessary to produce a red colouration with 1 grm. of potassium iodide

M. Wegner† determines formic acid in the presence of acetic acid by decomposing it with concentrated sulphuric acid and collecting the carbon monoxide given off in a nitrometer.

**Analysis of Oxalic Acid.**—*Commercial oxalic acid* is not very often found adulterated, and impurities due to careless manufacture are not, as a rule, great. The amount of pure acid (in the absence of other acids and acid salts) may be accurately determined by standard alkali and phenolphthalein. 2 grms. is a convenient quantity to take for titration. Each c.c. of normal caustic soda corresponds to 0.063 grm. of crystallised oxalic acid,  $C_2H_2O_4, 2H_2O$ .

*Oxalic acid and oxalates* may be determined in several ways by conversion in the first place into calcium oxalate. In the absence of other acids which are precipitated by calcium salts the liquid may be neutralised by ammonia and calcium chloride added. If phosphates, tartrates, sulphates, &c., are present the solution must be made slightly acid with acetic acid before adding the calcium chloride.

The calcium oxalate obtained may be converted into calcium carbonate by gentle ignition, and weighed as such; or it may be converted into calcium sulphate. It is better, however, to proceed according to one of the following methods:—

1. Wash the calcium oxalate well with hot water, transfer to a crucible, and ignite. The oxalate is converted into carbonate and, possibly, partly into oxide; but the results are the same in either case. The ignited residue is treated with an excess of normal nitric acid; the solution boiled and titrated back with normal caustic soda. Each c.c. of normal acid consumed = 0.063 grm.  $C_2H_2O_4, 2H_2O$ .

2. Instead of drying and igniting the calcium oxalate, it may be transferred direct to a beaker, treated with water and dilute sulphuric acid and titrated with potassium permanganate, as described below.

**Titration of Oxalic Acid and Oxalates by Permanganate.**—In the absence of other oxidisable bodies, this forms a ready means of estimating oxalic acid, either free or combined. A decinormal solution of potassium permanganate containing 3.16 grms of  $KMnO_4$  per litre is prepared by taking rather more than that amount of the salt and standardising the solution with *pure* oxalic acid. For this purpose exactly 0.315 grm. of pure oxalic acid (or 50 c.c. of  $\frac{N}{10}$  solution) is taken and dissolved in about 50 c.c. of water. About 50 c.c. of dilute sulphuric acid are added, the liquid heated to 50° or 60° C. and titrated with  $\frac{N}{10}$  permanganate until a permanent pink colouration appears. If the permanganate is strictly decinormal 50 c.c. will be required to produce this effect. If found too strong, it is diluted in the same manner as described under standard solution of sulphuric acid (p. 752).

The sample of oxalic acid or oxalate to be determined is then treated in exactly the same way. Each c.c. of  $\frac{N}{10}$  permanganate corresponds to 0.0063 grm. of  $C_2H_2O_4, 2H_2O$ .

**Impurities in Oxalic Acid.**—Mineral salts are detected by igniting a portion of the sample; sulphates by dissolving in water and adding barium chloride

\* *Journ. Soc. Chem. Ind.*, 1900, p. 568.

† *Ibid.*, 1903, p. 1019.

and hydrochloric acid. Organic matter, other than oxalic acid, is present if the sample blackens on heating alone, or with concentrated sulphuric acid.

**Analysis of Tartaric Acid and Tartrates.**—The free acid is readily determined by normal caustic soda and phenolphthalein. About 2 grms. may be taken for analysis.

Each c.c. of normal alkali = 0.075 gm. tartaric acid.

*Impurities* in tartaric acid may be detected as in oxalic acid.

Tartaric acid is sometimes, though not often, found adulterated with bisulphate of potash and alum.

Pure tartaric acid leaves no residue on ignition.

Acid potassium tartrate ( $\text{KHC}_4\text{H}_4\text{O}_6$ ) occurs in various forms, as *cream of tartar*, *argol*, and *tartar*.

Warrington, who, with Grosjean, has published many valuable papers on tartaric and citric acids, recommends the following methods for determining the value of commercial tartrates:—

1. (a) 1 gm. of the finely-powdered sample is heated with a little water and treated with about three-fourths of the total amount of  $\frac{N}{2}$  caustic soda required to neutralise it. The liquid is boiled, and, when nearly cold, neutralised exactly with a further quantity of  $\frac{N}{2}$  soda, using phenolphthalein as indicator.

$$1 \text{ c.c. of } \frac{N}{2} \text{ alkali} = 0.0376 \text{ gm. } \text{KHC}_4\text{H}_4\text{O}_6.$$

(b) 1 gm. of the sample is ignited in a platinum crucible at a low red heat. The ash is transferred to a beaker or porcelain basin, and treated with a slight excess of  $\frac{N}{2}$  sulphuric acid, and the liquid heated to boiling. The excess of acid is then determined by  $\frac{N}{2}$  alkali with methyl orange. From the alkalinity of the ash of 1 gm. of tartar is subtracted the acidity of 1 gm. of unburnt tartar (both in terms of  $\frac{N}{2}$  alkali), when the difference represents the neutralising power of the bases existing as *neutral tartrates*. 1 c.c. of  $\frac{N}{2}$  acid is in this case equivalent to 0.015 gm. of tartaric acid as *neutral tartrate*, or 0.0226 gm. of  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ .

*Example.*—(a) 1 gm. of tartar neutralised 23.2 c.c.  $\frac{N}{2}$  NaOH.

$$\therefore 0.0376 \times 23.2 \times 100 = 87.23 \text{ per cent. } \text{KHC}_4\text{H}_4\text{O}_6.$$

(b) 1 gm. of the sample after ignition was treated with 50 c.c.  $\frac{N}{2}$   $\text{H}_2\text{SO}_4$  and boiled, when 24.5 c.c.  $\frac{N}{2}$  NaOH were required to neutralise excess of acid. 25.5 c.c. acid were consumed by ash of 1 gm.

$$\therefore 25.5 - 23.2 = 2.3 \text{ c.c. required for ash of neutral tartrate.}$$

$$0.0226 \times 2.3 \times 100 = 5.20 \text{ per cent. } \text{K}_2\text{C}_4\text{H}_4\text{O}_6.$$

In presence of carbonates, this process does not give the separate amounts of acid and neutral tartrates, but the correct amount of total tartaric acid is obtained.

2. The following process depends upon the conversion of all the tartaric acid present into acid potassium tartrate.

About 3 grms. of the sample are heated with a little water, and digested for about twenty minutes with an excess of neutral potassium oxalate, whereby any calcium tartrate is converted into oxalate, with formation of potassium tartrate. From 1 to 2 grms. of potassium oxalate should remain in excess. The liquid is now nearly neutralised with caustic potash, filtered through a small filter, and the residue well washed. The filtrate and washings, containing the whole of the tartaric acid as normal potassium tartrate are concentrated to about 60 c.c.; 5 grms. of powdered potassium chloride are added, and the solution allowed to cool. A strong solution of about 3 grms. of citric acid is then added, and the mixture stirred continuously for about ten minutes. The acid potassium tartrate which is thus precipitated is collected on a filter and washed (preferably



by the aid of a filter pump) with a 5 per cent. solution of potassium chloride saturated with potassium bitartrate. The precipitate is transferred to the beaker in which the operation was conducted, dissolved in hot water, and titrated with normal alkali, using phenolphthalein as indicator.

Each c.c. = 0.150 grm. tartaric acid.

Scheurer-Kestner\* determines the total amount of tartaric acid in tartar as follows:—A weighed amount of the sample is digested with dilute hydrochloric acid and filtered. The filtrate is neutralised with caustic soda and treated with a slight excess of calcium chloride whereby the tartaric acid is precipitated as calcium tartrate. The precipitate is washed, dried, and ignited, and the resulting calcium carbonate estimated volumetrically with standard acid and alkali. 100 parts of  $\text{CaCO}_3$  correspond to 150 parts  $\text{C}_4\text{H}_6\text{O}_6$  or to 188 parts  $\text{KHC}_4\text{H}_4\text{O}_6$ .

Goldenberg's hydrochloric acid method† for determining tartaric acid in tartar and argol is used to a great extent. 6 grms. of the sample are mixed with 9 c.c. of hydrochloric acid, specific gravity 1.10, kept at the ordinary temperature for one to two hours, gradually diluting with water up to 100 c.c. and filtered. 50 c.c. of the filtrate are boiled with 10 c.c. of a 30 per cent. solution of potassium carbonate and the solution again filtered from precipitated lime. The filtrate and washings are evaporated down to 100 c.c., acidified with 2.5 c.c. of glacial acetic acid, and 100 c.c. of pure alcohol added. Potassium bitartrate is thus precipitated, and, after standing some time, it is filtered through a small filter and washed with alcohol until free from acetic acid. The filter and precipitate are then returned to the precipitating vessel, treated with boiling water, and titrated with normal caustic soda. Every molecule of bitartrate found corresponds to one molecule of tartaric acid present in the substance tested.

Moszczenski‡ criticises Goldenberg's process and recommends treating the sample of tartar with dilute sulphuric acid followed by strong alcohol. An aliquot part of the filtered alcoholic solution is mixed with alcoholic potassium acetate whereby potassium bitartrate is precipitated. This is filtered off, washed with strong alcohol, and titrated with normal caustic soda.

*Impurities.*—In addition to natural impurities, ground tartar and argol are frequently found adulterated with various substances, such as *alum* and *bisulphate of potash*, and occasionally with *gypsum* and *chalk*.

*Tartar substitute* (*Tartar cake*, &c.) usually consists simply of a mixture of crude sodium sulphate and bisulphate. It is commonly prepared by heating a mixture of salt cake and sulphuric acid. Some varieties contain oxalates and others consist of mixtures of sodium sulphates and real tartar.

**Analysis of Citric Acid.**—Citric acid in the free state is estimated by titration with  $\frac{N}{2}$  soda and phenolphthalein (litmus is not suitable). 1 c.c. of  $\frac{N}{2}$  alkali = 0.014 grm. of crystallised citric acid,  $\text{C}_6\text{H}_8\text{O}_7$ ,  $\text{H}_2\text{O}$ . Citric acid is liable to the same impurities and adulterations as tartaric acid (*q.v.*).

*Tartaric acid* may readily be detected by treating the sample with concentrated sulphuric acid, and heating the mixture in the water oven for about half an hour. Pure citric acid undergoes practically no change, whereas tartaric acid blackens. One per cent. of tartaric acid in citric acid may be thus detected. For determining the amount of tartaric acid in citric acid, Allen's§ process is to be recommended. It depends upon the precipitation of acid potassium tartrate by a solution of potassium acetate in proof spirit.

\* *Comptes Rend.*, lxxxvi., p. 1024.

† *Chemiker-Zeitung*, 1888, p. 390; 1889, p. 356.

‡ *Journ. Soc. Chem. Ind.*, 1898, p. 215.

§ *Chem. News*, vol. xxxi., p. 277.

*Oxalic acid* may be detected by neutralising with ammonia and adding acetic acid and calcium chloride, when, if oxalic acid be present, a precipitate of calcium oxalate will be formed.

**Analysis of Lactic Acid.**—Lactic acid is of great importance in the mordanting of wool with bichromates. In the absence of other acids, the percentage of lactic acid in a commercial sample may be ascertained by titrating in the cold with standard caustic soda, with phenolphthalein as indicator. Lactic anhydride is usually present in commercial samples of lactic acid, and this is not estimated by titration in the cold. By boiling with excess of caustic soda, the anhydride is converted into lactic acid and can be determined by titrating back with standard acid. It is convenient to take 10 grms. of the sample and make up to 500 c.c. 25 c.c. are then titrated in the cold with  $\frac{N}{5}$  caustic soda. The number of c.c. required gives the amount of lactic acid present. A known excess of the standard alkali (about double the amount already used) is then added and the liquid boiled for about 20 minutes. The solution is now titrated back with  $\frac{N}{5}$  acid until neutral to phenolphthalein and the additional amount of caustic soda consumed during boiling calculated into lactic anhydride. 1 c.c.  $\frac{N}{5}$  caustic soda = 0.018 gm. lactic acid and 0.0144 lactic anhydride.

F. Ulzer and H. Seidel\* estimate the amount of lactic acid by converting it into oxalic acid in an alkaline solution. 1 gm. of the sample is dissolved in 100 c.c. of water containing 3 grms. of potassium hydrate, and, with continual shaking, a 5 per cent. solution of potassium permanganate is gradually added until the liquid has no longer a green but a bluish-black colour. The liquid is boiled, decolourised with hydrogen peroxide or sulphurous acid, and filtered. A portion of the filtrate is acidified and titrated with standard permanganate solution. It is assumed that the lactic acid has been oxidised in accordance with the equation:— $C_3H_6O_3 + 5 O = C_2H_2O_4 + CO_2 + 2 H_2O$ . It is obvious that in using this method, samples must not contain oxalic acid or such bodies as glycerine, which are oxidised to oxalic acid in alkaline solution.

## ANALYSIS OF WATER.

It need scarcely be stated that the methods of analysis here given refer only to water for dyeing, scouring, and other technical purposes. The analysis of water for drinking purposes is quite a distinct subject.

A few qualitative methods of testing for the more commonly occurring substances in waters are given on p. 76.

*Determination of Suspended Matter.*—If, on shaking, the sample is found to contain a considerable amount of suspended matter, 1 or 2 litres, according to the apparent amount of insoluble substances present, may be filtered through a filter paper which has been previously dried in the steam-bath until of constant weight. When the water has passed through the filter, it is removed, and this portion, together with the whole of the remaining water (which should be filtered at once through an unweighed filter paper) afterwards used in the subsequent determinations.

The insoluble matter on the weighed filter paper is well washed with cold distilled water, and dried in the water-bath until of constant weight.

The increase in weight of the filter paper gives the total suspended matter.

The *insoluble mineral matter* may be estimated by igniting the filter paper and its contents in a platinum basin, and heating over a Bunsen flame until a constant weight is obtained.

Non-volatile residue = insoluble mineral matter.

\* *Journ. Chem. Soc. (Abs.)*, 1897, 2, p. 389.

The total insoluble matter, minus the insoluble mineral matter, gives the suspended organic and volatile matter.

**Total Solid Matter.**—About a litre of the water, accurately measured, is evaporated to dryness in a platinum dish, and dried at 105° C. in an air-oven until no further loss in weight takes place. The weight of this residue in grms. per litre multiplied by 70 equals grains per gallon of total solid matter.

**Organic Matter and Combined Water.**—The residue is gently ignited over a low flame and the loss in weight noted. Calcium and magnesium carbonates may be partially converted into oxides in this operation, and should be re-carbonated by moistening with a little ammonium carbonate, drying, and again igniting.

**Total Mineral Matter** is represented by the weight of residue obtained after gentle ignition. In many cases this is a check upon the results of the analyses of the various constituents. In other cases, however, where such salts as calcium nitrate, magnesium carbonate, &c., are present in the water in considerable quantities, the weight of the total saline matter obtained direct is of little value.

**Silica.**—The ignited residue obtained from a litre of water is treated with dilute hydrochloric acid, taking care to cover the dish with a clock-glass to guard against loss from effervescence. The under side of the glass is rinsed with distilled water into the dish, and the solution evaporated to dryness. It is then heated in an air-bath to a temperature of about 130° for an hour to render the silica insoluble. When cold, strong hydrochloric acid is added in rather more than sufficient quantity to moisten the residue, and after standing 15 to 20 minutes, water is added and the liquid heated to boiling. It is then passed through a small iron-free Swedish filter, the residue of silica well washed, dried, ignited, and weighed. Grammes per litre multiplied by 70 equals grains per gallons.

**Alumina and Oxide of Iron.**—To the filtrate and washings from the silica, which need not measure more than about 100 c.c., a slight excess of ammonia is added and the liquid kept near the boiling point until the smell of ammonia has disappeared. It is then filtered through a small Swedish paper, washed, dried, gently ignited, and weighed.

**Oxide of Iron.**—The ignited precipitate of oxide of iron and alumina is dissolved in a little concentrated hydrochloric acid and diluted with water to 100 c.c. If the amount of iron is considerable (which is seldom the case), the iron may be reduced by metallic zinc and titrated by  $\frac{N}{50}$  (0.632 grm. per litre) permanganate (see p. 792), or by direct titration with titanous chloride (see p. 793). The amount of iron is usually so small that it is best estimated by means of colour-titration, with either potassium ferrocyanide or thiocyanate.

**Estimation of Iron by Ferrocyanide.**—A weak standard solution of iron is prepared so as to contain 0.00001 grm. of Fe per c.c. For this purpose 0.7 grm. of ferrous ammonium sulphate (= 0.1 grm. Fe) is dissolved in a little water, acidulated with sulphuric acid, and oxidised either with nitric acid or potassium permanganate, and diluted to a litre. 100 c.c. of this solution are then further diluted to a litre.

The operation may be conveniently performed in Nessler tubes. 10 to 50 c.c. of the solution containing the ferric oxide (made up to 100 c.c., as above described), are put into a Nessler tube; 1 c.c. of strong hydrochloric acid (free from iron) and 1 c.c. of a 2 per cent. solution of potassium ferrocyanide added, and filled to the 100 c.c. mark with distilled water. A quantity of the weak iron solution judged sufficient to produce the same depth of colour (1 to 20 c.c.) is run into a similar tube, mixed with the same quantities of acid and ferrocyanide, and made up to 100 c.c. After allowing a few minutes for the colour to develop, the cylinders are compared, and a fresh experiment made with more

or less of the standard iron solution as may be required. Before adding the ferrocyanide, it is better to dilute the standard iron solution to the same extent as the liquid under examination. Nitric acid may be used in place of hydrochloric, but it is important to note that it should be free from nitrous acid. Nitric acid which has been exposed to light produces a green or greenish-yellow colouration with iron and ferrocyanide, instead of a blue. In place of Nessler tubes, the colorimeter may be used for this purpose.

*Example.*—The precipitate containing ferric oxide from a litre of water was dissolved in acid and diluted to 100 c.c. 10 c.c. of this solution produced the same depth of colour with potassium ferrocyanide as 6 c.c. of the standard iron solution. One litre of the water, therefore, contains  $0.00006 \times 10 = 0.0006$  gram. of Fe; = 0.042 grain of Fe = 0.06 grain of  $\text{Fe}_2\text{O}_3$  per gallon.

**Estimation of Iron by Thiocyanate.**—This method is recommended by A. Thompson.\* Exactly the same mode of working may be followed as with ferrocyanide. It is an exceedingly delicate reaction; 1 part of iron can be recognised in 50,000,000 parts of water.

**Lime.**—The filtrate and washings from the iron and alumina precipitate are made slightly ammoniacal, and the calcium precipitated as oxalate by ammonium oxalate. The liquid should be kept hot for some hours and filtered. The precipitate, after being washed, may be taken direct to a weighed crucible, heated at first very gently and then more strongly. When the carbon of the filter has completely disappeared the crucible is cooled and carefully treated with a drop or two of pure sulphuric acid, and again heated to drive off the excess. 136 parts of  $\text{CaSO}_4 = 56$  parts of CaO.

The lime may be more quickly determined by taking the well-washed precipitate of calcium oxalate direct to a beaker or basin with about 100 c.c. of water, adding 50 c.c. dilute sulphuric acid, warming to  $50^\circ$  to  $60^\circ$  C., and titrating with  $\frac{N}{10}$  potassium permanganate.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.0028 \text{ gram. of CaO.}$$

**Magnesia** is determined in the filtrate and washings from the calcium oxalate precipitate. The liquid should be concentrated by evaporation to about 40 c.c. A drop or two of a strong solution of citric acid is added, and when cold an excess of ammonia and about 5 to 10 c.c. of a solution of sodium phosphate added. After standing 12 hours, the liquid is filtered, and the precipitate, consisting of ammonium-magnesium phosphate, well washed with a mixture of 1 part of strong ammonia and 6 parts of water in the cold. The filter and precipitate are dried and ignited separately in a crucible, at first gently, afterwards intensely, and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$ . 111 parts of this precipitate = 40 parts of MgO.

H. R. Procter† recommends Pfeifer's volumetric method for the estimation of magnesia. 100 c.c. of the water is neutralised with  $\frac{N}{10}$  acid in the presence of Alizarin at the boil. A known quantity of clear limewater, at least 50 per cent. in excess of that required for precipitating the magnesia present, is measured into a 200 c.c. flask. The hot neutralised solution is rinsed in with boiling distilled water and made up with the latter to about 5 c.c. above the mark to allow of contraction in cooling. The flask is stoppered and well shaken. When the precipitate has settled and the liquid cooled down to the mark, 100 c.c. are withdrawn and titrated back with  $\frac{N}{10}$  acid. The difference between the acid consumed and that required for half the amount of limewater added represents the magnesia, in terms of  $\frac{N}{10}$  acid in 50 c.c. of water.

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0.002 \text{ gram. MgO.}$$

\* *Journ. Chem. Soc. (Tr.)*, 1885, p. 493.

† *Journ. Soc. Chem. Ind.*, 1904, p. 9.

**Potash and Soda.**—The alkalis are best determined in a fresh portion of the water. One litre is acidulated with hydrochloric acid, and concentrated to about 150 c.c. The sulphuric acid, iron, alumina, and magnesia are removed by boiling with a little pure baryta water. The excess of barium and the lime in the filtrate are removed by digesting with ammonium carbonate and oxalate. The filtrate is evaporated to dryness and gently ignited; the residue treated with water, filtered from any insoluble matter, and the solution evaporated to dryness with hydrochloric acid. The residue of alkaline chlorides thus obtained is again gently ignited and weighed. If it be desired to determine the separate amounts of potash and soda present, the former may be estimated by platinum chloride, or the chlorine may be estimated in the mixed chlorides, and the potash and soda ascertained by calculation (see *Analysis of Potash Salts*, p. 758).

**Sulphuric Acid as Sulphates.**—A litre of water is acidulated with hydrochloric acid, evaporated to about 100 c.c., and a slight excess of barium chloride added. The precipitate is collected on a small filter, dried, ignited, and weighed as  $\text{BaSO}_4$ . 233 parts of  $\text{BaSO}_4 = 80$  parts of  $\text{SO}_3$ .

**Chlorine** is readily determined volumetrically by silver nitrate and potassium chromate. A convenient strength of silver nitrate is a solution containing 4.788 grms. per litre, each c.c. of which = 0.001 grm. Cl. If  $\frac{N}{10}$  silver nitrate is used, each c.c. = 0.00355 grm. Cl. From 100 to 500 c.c. of the water are measured into a porcelain basin, a drop or two of neutral potassium chromate added, and the liquid titrated with the standard silver nitrate solution, until the pure yellow colour changes to an orange-yellow.

**Total Alkalinity.**—500 c.c. are placed in a porcelain basin and titrated with  $\frac{N}{10}$  sulphuric acid, using either methyl orange or lackmoid as indicator. It is usual to express the alkalinity in terms of calcium carbonate.

$$1 \text{ c.c. } \frac{N}{10} \text{ H}_2\text{SO}_4 = 0.005 \text{ grm. CaCO}_3$$

**Alkaline Carbonates.**—250 to 500 c.c. are boiled for half an hour in a porcelain beaker or basin and filtered, the filter being washed with well boiled distilled water. The filtrate is then titrated with  $\frac{N}{10}$  sulphuric acid as above.

$$1 \text{ c.c. } \frac{N}{10} \text{ acid} = 0.0053 \text{ grm. Na}_2\text{CO}_3$$

**Carbonic Acid, Combined,** is determined at the same time as the total alkalinity (see above).

$$1 \text{ c.c. of } \frac{N}{10} \text{ acid} = 0.0022 \text{ grm. of CO}_2$$

**Carbonic Acid, Free, and as Bicarbonate.**—This determination is of great importance for ascertaining the amount of lime or caustic soda required to be added in order to "soften" water. Pettenkofer's method is recommended for this purpose. 100 c.c. of the water are put into a flask with 3 c.c. of a strong solution of barium chloride, 2 c.c. of ammonium chloride, and 45 c.c. of a solution of barium hydrate of known strength. The flask is corked, the contents thoroughly shaken, and allowed to remain at rest for the precipitate of barium carbonate to subside. 50 c.c. of the clear liquid are then withdrawn, and titrated with decinormal nitric acid. The number of c.c. multiplied by 3, deducted from the number of c.c. required to neutralise 45 c.c. of barium hydrate direct, expresses the amount of  $\text{CO}_2$  in the liquid in terms of decinormal acid. Each c.c. of  $\frac{N}{10}$  acid = 0.0022 grm. of  $\text{CO}_2$  free, and as bicarbonate.

*Example.*—100 c.c. of water were treated as above. (45 c.c. of barium hydrate solution neutralised 35.1 c.c. of  $\frac{N}{10}$   $\text{HNO}_3$ .) 50 c.c. of the clear solution (= one-third of whole) neutralised 9.2 c.c. of  $\frac{N}{10}$  nitric acid.

$$35.1 - (9.2 \times 3) = 7.5 \text{ c.c. } \frac{N}{10} \text{ HNO}_3 \text{ equivalent to free CO}_2 \text{ in 100 c.c. of water.}$$

$$\therefore 0.0022 \times 7.5 \times 10 \times 70 = 11.55 \text{ grains of CO}_2 \text{ per gallon.}$$

Free carbonic acid, as distinct from that existing as bicarbonate, may be estimated by means of decinormal sodium carbonate in the presence of phenolphthalein, this indicator being neutral to sodium carbonate.

**Hardness.**—The hardness of natural water is due almost entirely to the presence of salts of lime and magnesia (p. 75) which form insoluble stearates, palmitates, oleates, &c., with the fatty acids of soaps. For many years the hardness of a water has usually been determined by means of a standard solution of soap in weak alcohol, but chemists are now gradually adopting the *acidimetric* process. Both methods will be here described, but for general purposes decided preference is to be given to the acidimetric process. The soap test, devised by the late Dr. Clark of Aberdeen, gives in many cases (with waters containing principally sulphate of lime, for example) accurate and reliable results, but in numerous other cases, especially with waters highly charged with magnesium salts and free carbonic acid, the test is unsatisfactory. With any kind of water, if the hardness exceeds 16° (with magnesium waters 7°), the lathering does not proceed regularly, and in order to obtain concordant results, it is necessary to dilute with distilled water. Regarding this matter, A. H. Allen\* writes:—

“This practice of diluting any hard water before titrating with soap solution raises the question: What is meant by the ‘hardness’ of water? Does it mean the soap-destroying power; or does it mean the proportion of calcium and magnesium compounds expressed in terms of calcium carbonate? If by the term ‘hardness’ the soap-destroying power of a water is to be understood, it seems very improper and unfair to dilute the water before making the determination. The laundress and manufacturer do not dilute the water they use, and hence to report a water as destroying as much soap as one containing, say, 30 grains of chalk per gallon, when, as a matter of fact, it does nothing of the kind, unless diluted before making the test, is misleading, and, in my opinion, is a practice which ought to be abandoned. On the other hand, if the ‘hardness’ is intended to represent the calcium and magnesium compounds in the water, the figures I have quoted suffice to show that the results are of the crudest possible character, quite unworthy of any one aspiring to the title of chemist.”

Although not to be recommended for general analytical purposes, the “soap-test” from its simplicity and rapidity is frequently of great service. When large quantities of water are being “softened” it is often necessary to make tests daily or more frequently. Again it is often required to make daily or hourly tests of the variations which take place in the hardness of the water from a well, stream, or other source. For these and similar purposes the soap-test is exceedingly useful.

**Hardness by Soap-test.**—Wanklyn’s method of working is perhaps the simplest, although for reasons mentioned above (and on p. 78), and in order that the results may be comparable with those obtained by the acidimetric method, the hardness of the water *per se* is not here taken into account. In other words, the degrees of hardness are intended to represent the number of grains of calcium and magnesium salts expressed in terms of calcium carbonate per gallon. According to Wanklyn’s system the degrees of hardness are equal to grains of calcium carbonate per gallon, plus one.

The *soap solution* is conveniently prepared by dissolving 10 grms. of pure white Castile soap in 600 c.c. of alcohol (90 per cent.) and diluting with water to a litre. This solution will probably be too strong and will require standardising. For this purpose a solution of *calcium chloride* is prepared by dissolving 1.11 grms. of the pure anhydrous salt in a litre of water. Or 1 grm. of pure

\* *J. urn. Soc. Chem. Industry*, 1888, p. 797. See also F. W. Richardson, *Journ. Soc. Dyers and Col.*, 1893, p. 194.

calcium carbonate is carefully dissolved in a slight excess of hydrochloric acid, the solution evaporated to dryness, the residue treated with water and evaporated to dryness, and finally dissolved in water and diluted to a litre.

*Standardising the Soap Solution.*—10 c.c. of the calcium chloride solution are introduced into a 10-oz. stoppered bottle and diluted with 60 c.c. of distilled water. The soap solution is added in small quantities (about 1 c.c.) at a time from a burette, and the bottle well shaken. When the lather begins to disappear somewhat slowly, smaller quantities are added at a time, and the bottle is placed on its side. The operation is complete when an unbroken lather remains permanent for five minutes. If the soap solution is of the correct strength 11 c.c. will have been required to produce this effect. If less than 11 c.c. the solution must be measured and carefully diluted with 50 per cent. alcohol until of the correct strength. The extra 1 c.c. is required to give a permanent lather with 70 c.c.\* of pure water only. The *total hardness* of a water is ascertained by taking 70 c.c. and titrating with the standard soap solution as above. The number of c.c. minus one equals grains of  $\text{CaCO}_3$  per gallon.

[The standard soap solution contains in each c.c. just sufficient soap to precipitate 1 milligramme of  $\text{CaCO}_3$ , and 1 milligramme bears the same relation to 70 c.c. as 1 grain to a gallon.]

If more than 16 c.c. (or more than 7 c.c., if much magnesia is present) are required, a smaller quantity of water should be taken and made up to 70 c.c. with distilled water.

*Temporary and Permanent Hardness.*—If a water undergoes no change in its soap-destroying power when boiled for some time, its hardness is said to be permanent, whereas, on the other hand, if the water becomes soft on boiling it is known as a temporary hard water. Both qualities are very frequently combined in the same water. The permanent hardness, due principally to sulphates of lime and magnesia, is determined by boiling 250 c.c. or 500 c.c. of water for half an hour, cooling quickly, and making up to the original volume with recently boiled and cooled water. 70 c.c. of the filtered solution are then titrated with soap as above. It is evident that the difference between the direct titration and that after boiling, represents the precipitated carbonates of lime and magnesia previously held in solution by carbonic acid. This is known as the *temporary hardness*. It should not be overlooked that calcium carbonate itself is soluble in *pure* water to the extent of about 2 grains per gallon. Consequently according to the general acceptance of the terms "temporary" and "permanent" the hardness of a water containing 2 grains of calcium carbonate per gallon is permanent.

*Hardness by the Acidimetric Process.*—There are various modifications of applying this test. The *total hardness* may be obtained as follows:—100 c.c. (or more) are treated with an excess of sodium carbonate and boiled down, nearly to dryness, in a platinum or porcelain dish. The liquid is passed through a small filter and the residue washed with a little boiling (previously well boiled) distilled water, until the filtrate is neutral. The main portion of the precipitated calcium and magnesium salts remains in the dish, to which the washed filter is now added with about 50 c.c. of distilled water. A drop or two of methyl orange or lackmoid is added and a slight excess of  $\frac{N}{10}$  nitric acid. After boiling a few minutes, the excess of acid is determined by  $\frac{N}{10}$  alkali. Each c.c. of  $\frac{N}{10}$  acid consumed equals 0.005 grm. of  $\text{CaCO}_3$ . The total amount of calcium and magnesium salts, expressed in terms of  $\text{CaCO}_3$ , is thus obtained. In the case of very "soft" waters, 200 or 500 c.c. should be taken, and  $\frac{N}{50}$  acid and alkali might be substituted for decinormal.

\*This is not strictly correct under all conditions, but for practical purposes it is sufficiently near.

For determining the *permanent* hardness, Hehner,\* evaporates a given volume of water to dryness, with a known amount of standard sodium carbonate in a platinum dish, extracts the residue with boiling distilled water, and determines the excess of sodium carbonate in the filtrate by weak standard acid. The sodium carbonate consumed represents the calcium and magnesium salts present in the water other than carbonates.

Pfeifer and Wartha† use a mixture of equal parts of sodium carbonate and hydrate instead of carbonate alone, in order to effect a complete precipitation of the magnesia. They also use Alizarin as indicator in place of methyl orange.

Gardner and Lloyd‡ find no advantage in using the mixture inasmuch as magnesium carbonate is quite insoluble in an excess of sodium carbonate.

The *temporary* hardness, due to *earthy carbonates* (in the absence of alkaline carbonates), may be readily ascertained by titrating 250 c.c. or 500 c.c. direct with  $\frac{N}{10}$  acid in a porcelain dish, using methyl orange or lackmoid as indicator. This has already been given under *Total Alkalinity* (p. 772).

In the case of an unknown water a given bulk should be boiled down exactly as described for the total hardness, omitting, however, the addition of sodium carbonate. The amount of standard nitric acid consumed by the precipitate thus obtained corresponds to calcium and magnesium carbonates.

O. Knöfler determines the combined carbonic acid, the lime and magnesia in one portion of the water as follows:—A mixture of methyl orange and phenolphthalein is used as indicator, which is yellow in neutral solutions and orange or red in either acid or alkaline solutions. A few drops of the indicator are added to 100 c.c. of the sample of water, which is titrated with  $\frac{N}{5}$  hydrochloric acid until faintly orange. Thus the combined carbonic acid is determined. The water is boiled for some time, so as to completely remove all carbon dioxide from the liquid. A *slight* excess of  $\frac{N}{5}$  alcoholic caustic soda is then added and the liquid boiled again. (Alcoholic soda is used to avoid the introduction of carbonic acid.) The hot solution is rapidly filtered and the precipitate washed with boiling water. In the filtrate the excess of caustic soda is neutralised with  $\frac{N}{5}$  hydrochloric acid; and thus the number of c.c. of  $\frac{N}{5}$  caustic soda consumed determines the amount of magnesia present. An excess of  $\frac{N}{5}$  sodium carbonate is now added to the neutralised water, which is again boiled and filtered. The filtrate is again neutralised with  $\frac{N}{5}$  hydrochloric acid, and the number of c.c. of  $\frac{N}{5}$   $\text{Na}_2\text{CO}_3$  actually required represents the amount of lime in the water.

On account of the slight solubility of earthy carbonates, already mentioned, in water *free* from carbonic acid, the carbonates obtained by the acidimetric method will not correspond exactly with the temporary hardness obtained by the soap test. The terms “temporary” and “permanent hardness” might, however, with advantage, be altogether dispensed with, and *hardness due to carbonates*, and *hardness due to salts other than carbonates* substituted. Permanent hardness gives the impression that it cannot be removed, whereas, as a matter of fact, sulphates may be removed almost as easily as carbonates, although not by boiling.

\* *Analyst*, 1883, p. 77.

† *Zeits. angew. Chem.*, 1902, p. 198.

‡ *Journ. Soc. Chem. Ind.*, 1905, p. 394.



## ANALYSIS OF SOAP.

In many cases of soap analysis, it is merely necessary to estimate the amount of *water*, *fatty acids*, and *total alkali*. It is frequently of importance, however, to determine the amount of combined and uncombined alkali as well as uncombined fat.

A complete analysis would include the following determinations:—Water, uncombined fat, combined fatty acids (calculated as anhydrides), glycerin, resin, combined alkali, caustic alkali, sodium or potassium carbonate, chloride, sulphate and silicate, insoluble matter (clay, sand, oxide of iron, &c.).

In addition to these determinations, it is often necessary to make an examination of the fatty acids in order to ascertain the kind of oils and fats which have been used in manufacturing the soap.

In taking portions for analysis, sections should be cut across the centre of a bar in the case of hard soaps, and the outer portions of a soft soap should be removed. The different weighings should be made at one time in order to guard against any irregularity caused by the sample losing water.

**Water.**—The usual method is to weigh from 3 to 5 grms. in the form of thin shavings on a clock-glass or porcelain basin, and dry in an air-bath at a temperature of 110° until the weight is fairly constant. In the case of soft potash soap, a small glass rod should be weighed with the dish so that the soap may be stirred from time to time. Hard soaps require from two to four hours, but soft soaps frequently a much longer period.

Watson Smith\* recommends the following modification:—From 5 to 10 grms. of soap in thin shavings are weighed into a counterpoised crucible containing a piece of glass rod flattened at the upper end and rough and jagged at the lower extremity. The crucible is placed on a sand bath which is gently heated by a Bunsen burner; the contents being continually stirred and turned over with the glass rod. The end of the operation is ascertained by removing the lamp and holding a piece of glass (a watch-glass) over the crucible. When no more moisture becomes visible on the glass, the crucible is placed in a desiccator, cooled and weighed. Even if the soap burns a little, so penetrating is the odour of burnt soap that it will be immediately detected, and the loss thus caused is usually quite inappreciable. The operation can be performed in about twenty minutes. With potash soaps and others containing glycerin, the results are not satisfactory, since it is difficult to ascertain exactly when the water is all given off.

**Total Alkali.**—5 grms. are dissolved in about 200 c.c. of hot water, and with either methyl orange or cochineal as indicator, titrated with  $\frac{N}{8}$  sulphuric acid, each c.c. of which corresponds to 0.0062 gm.  $\text{Na}_2\text{O}$  or 0.0094 gm.  $\text{K}_2\text{O}$ . The fatty acids set at liberty have no action upon either of these indicators.

If the amount of *potash* be required when both potash and soda are present, a given weight of soap is decomposed with hydrochloric acid and the filtered solution treated with platinum chloride as on p. 758.

**Uncombined Alkali.**—This may exist in a soap either as *caustic* or *carbonate*, or both. The best method of analysis consists in extracting the dry soap with strong alcohol. About 3 grms. in fine shavings are weighed and dried in a water oven for about two hours. A water oven is preferable to an ordinary air-bath, since any caustic alkali which may be present is less liable to be converted into carbonate during the process of drying. In order to avoid this source of error altogether it is necessary to use a specially constructed bath arranged to prevent access of carbon dioxide. After drying, the soap is placed in a plaited filter or extraction thimble and introduced into a Soxhlet's tube, the

\* *Journ. Soc. Dyers and Col.*, 1884, p. 31.

lower end of which is connected to a small wide-mouthed flask containing pure alcohol, to which has been added a few drops of phenolphthalein and sufficient caustic potash (a drop or two of  $\frac{N}{10}$  KHO will usually suffice) to render the liquid faintly pink. The upper extremity of the Soxhlet's tube is connected with an inverted Liebig's condenser and the small flask immersed to the neck in water, which is kept at or near the boiling point. The flask may be heated direct on wire gauze over a small flame. The alcohol boils and the vapour condenses in the Soxhlet's tube. A portion of the soap and caustic alkali (if present) dissolves, and the solution flows over by means of the small siphon into the flask. The operation must be continued until the whole of the soap has dissolved. The time required varies considerably, according to the nature of the soap and the rate at which the alcohol distils. From two to four hours will be required on an average. The alcohol solution contains the pure soap and any glycerin and caustic alkali which may be present. The solution will be pink if caustic alkali is present. It is titrated with  $\frac{N}{10}$  acid until the colour disappears. Each c.c. = 0.004 grm. NaHO or 0.0056 grm. KHO. The residue insoluble in alcohol may contain, in addition to sodium or potassium carbonate, chlorides, sulphates, silicates, and insoluble matter. It is dissolved in water and titrated with  $\frac{N}{10}$  sulphuric acid and methyl orange. Each c.c. = 0.0053 grm.  $\text{Na}_2\text{CO}_3$  or 0.0069 grm.  $\text{K}_2\text{CO}_3$ . For a more complete analysis of the residue see Leeds' scheme (p. 780).

Uncombined alkali is sometimes determined by precipitating a solution of soap with a strong solution of pure sodium chloride and titrating the filtrate with standard acid. The results are not accurate as pointed out by C. R. A. Wright and C. Thomson,\* but, excepting with soaps made from cocoa-nut and palm oil, fairly approximate figures are quickly obtained.

**Combined Alkali**—The alkali existing as carbonate (also silicate, if present) and caustic is subtracted from the total alkali, when the difference gives the amount of alkali combined with fatty acids as soap. The combined alkali may also be determined in the alcoholic solution after neutralising any free caustic alkali or free fatty acid in the presence of phenolphthalein. Water is added to the solution which with a few drops of methyl orange is titrated with standard acid. The acid thus consumed corresponds to combined alkali. The combined alkali may further be calculated from the amount of standard alcoholic potash required to neutralise the liberated fatty acids in the method described below. The total alkali having been determined, this method affords a means of estimating the uncombined alkali by difference.

**Fatty Acids.**—In a careful determination of all the other constituents of a soap, the fatty acids (or rather anhydrides), as recommended by Watson Smith,† may conveniently and with accuracy be ascertained by difference.

A method commonly used in practice, consists in decomposing a solution of 5 grms. of soap with sulphuric or hydrochloric acid. If the liberated fatty acids are soft a weighed amount of hard white wax or paraffin is added, and when cold the cake is carefully removed, dried, and weighed. It is often difficult to remove the whole of the fatty acids completely from the beaker, and in some cases a considerable portion of the fatty acids is soluble in water. This difficulty may be partially overcome by adding salt to the liquid. Or the amount of fatty acid in the liquid may be approximately ascertained by dividing the solution into two parts; titrating one portion with caustic soda and methyl orange and the other with caustic soda and phenolphthalein. The difference between the two titrations will give the amount of fatty acids present in terms of standard soda.

A preferable plan to the above for estimating fatty acids is the following:—

\* *Journ. Soc. Chem. Ind.*, 1885, p. 625.

† *Journ. Soc. Dyers and Col.*, 1884, p. 31.

About 3 grms. of the soap are dissolved in 50 to 60 c.c. of water and introduced into a stoppered separator of a capacity of 200 c.c. The soap is decomposed with a slight excess of hydrochloric acid, and when cold about 50 c.c. of ether added and the whole well shaken. When the two liquids have separated, the acid solution is run off and the ether solution washed two or three times in the separator with cold distilled water. The solution of fatty acids is then carefully poured into a small weighed wide-mouthed flask, and the separator well rinsed out with pure ether. The ether is distilled off and the residue of fatty acids dried in a water oven and weighed. In order to get rid of water (usually present in the residue) a little strong alcohol is added before the flask is put into the oven. By either process, the weight obtained will of course include any uncombined fat or unsaponifiable matter if present. This must be either estimated separately and deducted, or the dried soap must be previously treated with petroleum ether. The operation, however, is not often necessary in practice.

The fatty matter, weighed as free fatty acids, exists in the soap in combination with potash or soda. In a complete analysis it is, therefore, necessary to calculate the fatty acids into their corresponding anhydrides. In the majority of cases multiplying by 0.97 answers the purpose.

In the *Journal of the Society of Dyers and Colourists*, 1885, p. 58, Rawson describes a volumetric process for determining fatty acids in soap. The fatty acids from a weighed amount of soap are dissolved in about 50 c.c. of hot neutral alcohol, and, with phenolphthalein as an indicator, titrated with a standard solution of alcoholic potash. Knowing the saponification equivalent of the fatty acids (readily ascertained as described below), the percentage may be easily calculated. The operation may be readily performed by decomposing the soap with hydrochloric acid, and shaking up with ether in a separator, as already described, but instead of evaporating off the ether and weighing the residue of fatty acids, the ethereal solution is mixed with about 50 c.c. of neutral alcohol, and titrated direct with  $\frac{N}{2}$  alcoholic potash and phenolphthalein.

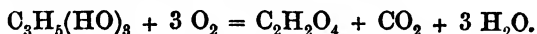
*Example.*—3 grms. of soap were decomposed by hydrochloric acid, and the liberated fatty acids neutralised 35 c.c. of  $\frac{N}{2}$  alcoholic potash. The saponification equivalent of the fatty acids was found to be 276; therefore 1 c.c. of  $\frac{N}{2}$  KHO = 0.0552 grm. of fatty acids.

$$\therefore \frac{0.0552 \times 35 \times 100}{3} = 64.40 \text{ per cent. of fatty acids.}$$

**Free Fat and Unsaponifiable Oil.**—This may be performed by extracting the dried soap in a Soxhlet's tube with light petroleum ether, which has been previously distilled on a water bath, but an objection to this plan is that soap is not quite insoluble in the volatile solvent, and a preferable method, as recommended by Allen, consists in dissolving the soap in water and shaking the solution with ether in a separator. When the liquids have separated (which frequently takes a considerable time), the aqueous solution of soap is run off, and the ether solution washed with water and poured into a tared flask. The ether is distilled and the residue dried and weighed. The aqueous solution of soap should be shaken up a second time with ether, unless the amount of unsaponified matter present is very small.

The ethereal solutions are combined, washed with water, poured into a flask, and the ether volatilised. Soap being somewhat soluble in ether may be present in the residue. Digesting with cold petroleum ether in small quantity, and subsequent filtration into a small wide-mouthed flask, distillation of the solvent and weighing the residue will rectify any error from this source. If this precaution be taken, it is allowable to add to the mixture of soap and ether during the first extraction, a little alcohol, which assists materially in causing a quicker separation of the aqueous and ethereal layers.

**Glycerin.**—In Leeds' scheme (p. 780) glycerin is determined gravimetrically, out at 100° C. glycerin volatilises somewhat freely, and the results are consequently too low. In the absence of sugar, it may be conveniently estimated by Benedikt and Zsigmondy's process,\* originally suggested by Wanklyn, and also investigated by Fox. The method is based upon the fact that when glycerin is oxidised in alkaline solution with potassium permanganate, it is converted into oxalic acid, carbon dioxide, and water :—



In the case of soap, 10 grms. are dissolved in water, and decomposed with dilute hydrochloric acid. The solution freed from fatty acids is diluted to 400 c.c., and made strongly alkaline with 10 to 15 grms. of caustic potash. A strong solution of potassium permanganate is added until the colour of the liquid changes from green to bluish-black. The mixture is boiled for about an hour, when the excess of potassium permanganate is destroyed by the addition of a strong solution of sodium sulphite, and the liquid filtered. The filtrate is acidulated with acetic acid and boiled, and the oxalic acid present precipitated by calcium acetate. The precipitate of calcium oxalate thus obtained may contain silica and calcium sulphate, and cannot, therefore, be weighed as carbonate. The precipitate may be ignited, and the lime estimated by titration with standard nitric acid and caustic soda, as on p. 766; or, preferably, the calcium oxalate is dissolved direct in dilute sulphuric acid, and the oxalic acid estimated by titration with  $\frac{N}{10}$  permanganate, as on p. 766. 56 parts of CaO, or 126 parts of  $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  correspond to 92 parts of glycerin.

**Resin.**—Gladding's method (see Leeds' scheme, p. 780) has been extensively used for estimating resin in soap, although the process is open to several objections. It is necessary to make a considerably allowance for the solubility of silver *oleate*, and Wright and Thomson† have shown that for different fats this is by no means constant. Gladding makes an allowance of 0.00235 gm. for every 10 c.c. of ether solution evaporated.

E. Twitchell, in the *Journal of Analytical Chemistry* (1891, p. 379), describes a process which has been found to give very satisfactory results. 2 to 3 grms. of fatty and resin acids (obtained by decomposing soap with dilute HCl) are dissolved in ten times their volume of absolute alcohol in a flask, and dry HCl gas passed through in a moderate stream. The flask is set in a vessel containing water to keep it cool. The hydrochloric acid is rapidly absorbed, and after about forty minutes the ethers of the fatty acids separate and float on the surface. The flask is removed and allowed to stand half an hour longer, to ensure a complete combination of the alcohol and fatty acids. The liquid is diluted with five volumes of water, and boiled until the acid solution is clear, the ethers, with resin acids in solution, floating on the top. On cooling, some light petroleum-naphtha is added, and the whole transferred to a separator. The acid solution is run off, and the naphtha solution (about 50 c.c. in volume) washed with water. A solution of 0.5 gm. of caustic potash, 5 c.c. of alcohol, and 50 c.c. of water is poured into the separator, and the whole agitated. The resin acids are thus saponified, and the ethers of the fatty acids remain in the naphtha. The solution of resin soap is run off and decomposed with hydrochloric acid, the resin collected, dried, and weighed. Instead of weighing the resin, it may be determined volumetrically by means of standard alkali. In this case, ether is used in place of naphtha, and the washing with water must be continued until the wash water is no longer acid. 50 c.c. of neutral alcohol are then added to the ethereal solution of resin and ethers in the separator, and with phenolphthalein as indicator, titrated with standard potash or soda. The

\* *Journ. Soc. Dyers and Col.*, 1885, p. 245.

† *Chem. News*, vol. liii. (1886), p. 165.

Weigh out 5 grammes. Dry at 110°. Loss corresponds to water.	
Treat with petroleum ether.	
Residue is soap and mineral constituents. Treat with alcohol.	
<p>Extract is soap (fatty anhydride, resin, and combined alkali), glycerin, and free alkali. Add two or three drops of phenolphthalein. If necessary, titrate with normal sulphuric acid.</p> <p>Add a large excess of water and boil off the alcohol. Decompose with excess of normal <math>H_2SO_4</math>. Boil, filter, and wash.</p> <p>Filtrate. — Combined soda and glycerin. Titrate with normal soda solution.</p> <p><math>H_2NO_4</math> After titration used evaporate to dryness on the water-bath. Treat with absolute alcohol. Evaporate the alcoholic solution to dryness in a tared dish and weigh as glycerin.</p> <p><math>Na_2O</math> soap. Calculate as <math>Na_2O</math>.</p>	<p>Residue — <math>Na_2CO_3</math>, <math>NaCl</math>, <math>Na_2SO_4</math>, sodium silicate, starch, and insoluble residue. Wash with 60 c.c. water.</p> <p>Filtrate. — <math>Na_2CO_3</math>, <math>NaCl</math>, <math>Na_2SO_4</math>, and sodium silicate. Divide into four equal parts.</p> <p><math>Na_2CO_3</math>. Titrate with normal <math>H_2SO_4</math> and calculate as <math>Na_2CO_3</math>.</p> <p><math>NaCl</math>. Titrate with <math>AgNO_3</math> or weigh as <math>AgCl</math>. Calculate as <math>NaCl</math>.</p> <p><math>Na_2SO_4</math>. Weigh as <math>BaSO_4</math>. Calculate as <math>Na_2SO_4</math>.</p> <p>Sodium silicate. Decompose with <math>HCl</math> and determine soda combined in silicate and silica.</p> <p>Residue. — Starch and insoluble residue. Dry the filter and weigh. The weight is the starch and insoluble residue. Starch. — Convert the starch into <math>C_6H_{12}O_6</math>. Titrate with Fehling's solution. Subtract the weight of starch found, and the difference is the insoluble mineral constituents.</p>
	<p>Residue is soap (fatty anhydride, resin, and combined alkali), glycerin, and free alkali. Add two or three drops of phenolphthalein. If necessary, titrate with normal sulphuric acid.</p> <p>Add a large excess of water and boil off the alcohol. Decompose with excess of normal <math>H_2SO_4</math>. Boil, filter, and wash.</p> <p>Filtrate. — Fatty acids and resin. Dry at 110° and weigh. Dissolve an aliquot part in 20 c.c. strong alcohol, and, using phenolphthalein as an indicator, saponify with soda in slight excess. Boil, cool, and add ether to 100 c.c. Decompose with <math>AgNO_3</math> by adding in fine powder, and shake well for ten minutes. Allow to settle.</p> <p>Precipitate is stearate, palmitate, and oleate of silver.</p> <p>Solution. — Re-estimate of silver. Filter 50 c.c. from the total 100 c.c. Decompose with 20 c.c. <math>HCl</math> (1:20). Allow the <math>AgCl</math> to settle, and evaporate an aliquot part of the ethereal solution in a tared dish. Dry at 110° and weigh. After applying correction for oleic acid, the weight corresponds to the resin. This weight subtracted from the combined weight of fatty acid and resin gives the fatty acids.</p>
<p>Extract is uncombined fat. Dry at 100° and weigh.</p>	

ethers of the fatty acids, under these conditions, are not affected by the alkali. The combining weight, or saponification equivalent, of the resin acids is taken at 346.

The scheme on opposite page for the complete analysis of soap (by A. R. Leeds) is taken from the *Chemical News*, vol. xlvi. (1883), p. 166.

**Examination of Fatty Matter in Soap.**—In the analysis of soap it is frequently desired to ascertain what kind of oils and fats have been used in its manufacture. This is much the most difficult part of the examination. Much information may generally be obtained from a determination of the saponification equivalent of the fatty acids; their specific gravity, and their melting and solidifying points. A few brief descriptions only will be here given. For fuller particulars, reference should be made to such works as Allen's *Commercial Organic Analysis*.

**Saponification Equivalent.**—About 5 grms. of the fatty acids (free from water) are dissolved in 60 to 70 c.c. of hot *neutral* alcohol, and, with phenolphthalein as indicator, titrated with  $\frac{N}{2}$  alcoholic potash. The weight in milligrammes of the fatty acids taken, divided by half the number of c.c. of  $\frac{N}{2}$  KHO required, gives the saponification equivalent.

**Specific Gravity** is best determined at 100° C. in a small Sprengel tube of a capacity of about 7 c.c. The weight of the dry tube and that of water contained in it at 15.5° are first ascertained. The tube is then filled with the melted fatty acid and placed in the mouth of a conical flask containing water, which is kept briskly boiling. The oil expands, and the excess flows out in drops from the capillary orifice. When the expansion ceases, any oil adhering to the orifice is carefully removed by filter paper, the tube removed, dried, cooled, and weighed. The weight thus obtained divided by the weight of water at 15.5° will give the density or specific gravity of the fatty acids at 100° compared with water at 15.5° as unity.

**Melting Point** of the fatty acids may be conveniently observed in the following manner:—A piece of quill-tubing is drawn out into a long capillary tube, which is cut into lengths of about 3 inches. One of these is dipped into the molten fatty acid, and a *small* quantity, occupying a space of about a tenth part of an inch, drawn up and allowed to solidify. After about an hour (not less) the tube is attached to the stem of a thermometer by means of a small india-rubber ring (a small bit cut off a piece of india-rubber tubing answers well) in such a manner that the fatty acid is close to the bulb. The thermometer with the tube is immersed in a small beaker of water, which is itself immersed in a conical flask or larger beaker filled with water. A Bunsen flame is placed under the vessel, and the thermometer and substance in the small tube carefully watched. The temperature should not be allowed to rise more than about  $\frac{1}{2}$ ° C. per minute. When the fatty acid melts (which is usually quite sharp) the temperature is at once observed and recorded.

**Solidifying Point** of fatty acids is best determined as described by Allen in the following manner:—A test tube, about 5 inches in length and  $\frac{3}{8}$  inch in diameter, is fitted with a ring or collar of cork, by which it is fixed in the mouth of an empty flask. The melted fatty acid is poured into the (warmed) tube till it is about two-thirds filled, and a delicate thermometer, previously warmed, is suspended freely in the liquid, so that the bulb may be wholly immersed. When the fatty acids begin to solidify at the bottom of the tube the thermometer must be attentively observed. The operator then stirs the contents of the tube slowly, by giving the thermometer a circular movement, first three times to the right, and then thrice to the left. The first effect of the agitation is to cause the thermometer to fall slightly, but subsequently a sensible rise takes place, and the mercury remains stationary for at least two minutes. The temperature thus indicated is the solidifying point of the sub-

stance, and the results obtained are remarkably constant. The following table, chiefly compiled from figures in Allen's *Commercial Organic Analysis*, will be found useful in drawing conclusions from data obtained by the above methods :—

SOURCE OF FATTY ACIDS.	Saponification equivalent or combining weight.	Specific gravity at 100° C. compared with water at 15·5°.	Melting point. °C.	Solidifying point. °C.
Olive oil, . . . .	279	·842	26	21
Cotton-seed oil, . . . .	277	·848	36	30-35
Rape oil, . . . .	320	·842	19·5	15-18
Linseed oil, . . . .	307	·853	18	13-17
Tallow, . . . .	273	·836	45	43-50
Palm oil, . . . .	270	·837	47-50	42-46
Cocoa-nut oil, . . . .	200	·835	24	20·5

The *scouring value* of soap is sometimes determined by means of a standard solution of calcium chloride. This solution (1·11 grms. CaCl<sub>2</sub> per litre) is prepared as described on p. 773 for determining the hardness of water. 5 grms. of soap are dissolved in 300 c.c. of 90 per cent. alcohol, and diluted to 500 c.c. with water. The operation is performed exactly in the same manner as in estimating the hardness of water. 10 c.c. of the calcium chloride solution are mixed with 60 c.c. of distilled water and titrated with the soap solution, until a permanent lather is obtained.

When two or more samples of soap are treated in this manner, the relative scouring value of the samples is inversely proportional to the number of c.c. consumed. The results are only approximately correct.

For further information on this subject a paper on "The Water-softening (or so-called 'Scouring') Power of Soap," by F. W. Richardson and A. Jaffe,\* may be consulted.

## ANALYSIS OF BLEACHING COMPOUNDS.

**Analysis of Chloride of Lime.**—This compound, known also as *bleaching powder*, is used in immense quantities in the bleaching of cotton, linen, and other vegetable fibres. It may be considered to consist practically of a mixture of calcium hypochlorite, calcium chloride, and calcium hydrate,† although in the dry state its composition is considered by Odling and Lunge to be represented by the formula Ca(OCl)Cl—that is, calcium-chloro-hypochlorite. Bleaching powder usually contains small quantities of calcium chlorate, and, in some cases, where sufficient care has not been taken in the manufacture, this compound may exist to the extent of from 8 to 10 per cent. The value of chloride of lime for bleaching purposes depends entirely upon the amount of available chlorine present. Chlorate of calcium is of no value as a bleaching agent.

Penot's method of analysis is based upon the conversion of an alkaline arsenite into an arsenate, when a solution of the former is added to a hypochlorite.



When sufficient of the sodium arsenite has been added to the bleaching powder solution the latter gives no further reaction for free chlorine with iodised starch paper.

\* *Journ. Soc. Chem. Ind.*, 1899, p. 998.

† *Journ. Soc. Dyers and Col.*, 1908, p. 81.

**Preparation of Decinormal Sodium Arsenite Solution.**—4.95 grms. of pure resublimed arsenious oxide and 25 grms. of pure sodium carbonate are dissolved in about 250 c.c. of water. The arsenious oxide must be in fine powder, and the liquid heated to boiling to promote solution. When quite clear it is cooled and diluted to one litre. The strength of the solution may be verified by titration with a carefully prepared *decinormal solution of iodine*. For this purpose 12.7 grms. of pure resublimed iodine are dissolved in the cold in a solution of 18 grms. of pure potassium iodide, and diluted to a litre. 10 c.c. of the arsenious solution are placed in a porcelain basin, and a few drops of starch solution added. The iodine solution is then run in from a burette with constant stirring until a permanent blue colour appears. In this and similar operations with iodine solution, it is not absolutely necessary to use starch as an indicator. The faintest excess (certainly less than  $\frac{1}{10}$  c.c.) of iodine, without starch, may be known by the liquid acquiring a pale yellow colour. If 10 c.c. are required, the solution is strictly decinormal.

**Titration of Bleaching-Powder Solution.**—10 grms. of the sample of bleaching powder are weighed out into a mortar, and rubbed into a thin cream with water. After allowing the coarser particles to subside, the turbid liquid is poured into a litre flask, and the particles in the mortar again ground up with more water. This is repeated three or four times, when the whole of the 10 grms. will have been transferred to the litre flask. Water is then added to the mark, and the flask well shaken. 50 c.c. of the turbid liquid, immediately after shaking, are withdrawn by means of a pipette and titrated with  $\frac{N}{10}$  arsenite solution until a drop of the liquid ceases to give a blue or violet colour with prepared iodised starch paper. This paper may be readily prepared by saturating filter paper with a solution made by boiling about  $\frac{1}{4}$  gm. of starch,  $\frac{1}{4}$  gm. of potassium iodide, and  $\frac{1}{10}$  gm. of sodium carbonate with 50 c.c. of water.

1 c.c. of  $\frac{N}{10}$  sodium arsenite = 0.00355 gm. Cl.

*Example.*—10 grms. bleaching powder made up to a litre, as above described. 50 c.c. (= 0.5 gm. sample) required 42.2 c.c. of  $\frac{N}{10}$   $As_2O_3$ .

$$\therefore \frac{0.00355 \times 42.2 \times 100}{0.5} = 29.95 \text{ per cent. of available chlorine.}$$

Bunsen's method depends upon the oxidation of sodium thiosulphate. It records some of the chlorine present as chlorate as well as hypochlorite: consequently, it is not so well adapted for the valuation of bleaching powder as Penot's method. If both methods are performed, the difference between the two results shows approximately the amount of chlorine present as chlorate.

A decinormal solution of *sodium thiosulphate* is prepared by dissolving 24.8 grms. of the pure crystallised salt,  $Na_2S_2O_3 \cdot 5H_2O$ , in a litre of water. This may be standardised either by a decinormal solution of iodine already described, or, preferably, by a decinormal solution of potassium bichromate, containing 4.917 grms. of  $K_2Cr_2O_7$  in a litre. For this purpose 25 c.c. of  $\frac{N}{10}$   $K_2Cr_2O_7$  are run into a porcelain basin; 10 c.c. of a 10 per cent. solution of potassium iodide, an excess of dilute hydrochloric acid, and about 200 c.c. of water are added. The thiosulphate solution is then gradually added from a burette until the solution is nearly colourless, when a little starch solution is added, and the titration continued until the blue colour disappears. If strictly decinormal, 25 c.c. of thiosulphate will be required, each c.c. of which corresponds to 0.00355 gm. Cl. In this reaction the bichromate liberates an equivalent amount of iodine from the excess of potassium iodide used.

**Titration of Bleaching Powder.**—20 c.c. of the solution prepared as above described (10 grms. per litre) are diluted with about 200 c.c. of water, and treated with 10 c.c. of potassium iodide solution and excess of acetic



acid. The liquid is then titrated with  $\frac{N}{10}$  thiosulphate exactly in the same manner as in standardising with bichromate.

*Example.*—20 c.c. of the bleaching powder solution, prepared as above described (= 0.2 grm. sample), required 18 c.c.  $\frac{N}{10}$  thiosulphate solution.

$$\therefore \frac{0.00355 \times 18 \times 100}{0.2} = 31.95 \text{ per cent. chlorine.}$$

The same sample showed 29.95 per cent. by Penot's method. Therefore about 2 per cent. chlorine was present as chlorate.

Lunge\* has devised a gasometric method depending upon the evolution of oxygen when a solution of bleaching powder or hypochlorite is mixed with peroxide of hydrogen.

**Free Lime.**—According to Cross and Bevan,† this is best estimated in the following way:—50 c.c. of the solution are diluted to 250 c.c.; 25 c.c. of this are placed in a beaker and diluted with water. 8 to 15 c.c. of a 3 per cent. solution of pure  $H_2O_2$  (Merck) are now added in about three portions—i.e., until the evolution of oxygen has ceased. A few drops of methyl orange solution are now added, and the solution is titrated with  $\frac{N}{10}$  acid until red. If the methyl orange is rapidly decolourised, this is a sign that hypochlorite is still present, and that not sufficient  $H_2O_2$  had been added.

Bleaching liquors and other hypochlorites may be analysed in exactly the same manner as chloride of lime.

**Analysis of Sodium Bisulphite.**—The principal bleaching agent for wool and silk is sulphurous acid, applied for the most part in the form of gas (sulphur dioxide) obtained by burning sulphur in "stoves" (see pp. 149, 160). Solutions of bisulphite of soda and other bisulphites are, however, now often used for this purpose. A large quantity of sodium bisulphite is also used in the preparation of the so-called "hydrosulphite" indigo vat.

**Sulphur Dioxide,  $SO_2$ .**—The best method of estimating the total amount of sulphur dioxide in sulphurous acid, sulphites, and bisulphites is by means of iodine, as described by Giles and Shearer in the *Journal of the Society of Chemical Industry*, 1884, p. 197. The older methods of analysis by means of iodine were liable to serious errors.

About 0.5 grm. of the sample (in the case of liquid sodium bisulphite it is better to take 10 c.c. and dilute to 500 c.c. with distilled water, which has recently been boiled and cooled), is weighed out and introduced at once into a known excess of decinormal iodine solution, and, after stirring, the excess of iodine is determined by a decinormal solution of sodium thiosulphate, as described under chloride of lime (p. 783).

The number of c.c. of  $\frac{N}{10}$  thiosulphate are deducted from the number of c.c. of  $\frac{N}{10}$  iodine taken and the remainder calculated to sulphur dioxide—

$$1 \text{ c.c. of } \frac{N}{10} \text{ iodine} = 0.0032 \text{ grm. of } SO_2.$$

*Example.*—10 c.c. liquid bisulphite of soda, sp. gr. 1.25, were diluted with recently boiled and cooled water to 500 c.c. 20 c.c. of this solution (= 0.4 c.c. or 0.5 grm. of sample) were introduced into a beaker containing 35 c.c. of  $\frac{N}{10}$  iodine. It was then found that 5.5 c.c. of  $\frac{N}{10}$  thiosulphate were required.

$$\therefore \frac{0.0032 \times 29.5 \times 100}{0.5} = 18.88 \text{ per cent. of } SO_2.$$

An excellent gravimetric process for estimating sulphur dioxide in sulphites is described by Giles and Shearer in the paper above mentioned.

Indicators used in acidimetry are very differently affected by sulphurous

\* *Journ. Soc. Chem. Ind.*, 1890, p. 22.

† *Ibid.*, 1890, p. 450.

acid and sulphites. With *phenolphthalein*, for example, normal sodium sulphite,  $\text{Na}_2\text{SO}_3$ , reacts neutral, whereas the acid sulphite (bisulphite),  $\text{NaHSO}_3$ , is neutral to *litmus*, *cochineal*, and *methyl orange*. With litmus and cochineal the reaction is uncertain, but with methyl orange it is sharp and distinct. *Normal sulphites* may, therefore, be readily determined by titrating with normal sulphuric acid and methyl orange.

*Free sulphurous acid* and sulphurous acid existing as bisulphite, may, on the other hand, be determined by using standard caustic soda and phenolphthalein. If commercial bisulphite of soda be diluted with water and a few drops of a solution of methyl orange added, the liquid will be red if *free sulphurous acid* is present, and the amount of standard alkali required to produce the neutral point, will be a measure of the sulphurous acid above that required to form bisulphite. If, on the other hand, the liquid is decidedly yellow, *normal sulphite* is present, the amount of which may be determined by standard acid.

**Analysis of Sodium Hydrosulphite.**—It is well known that solutions of hydrosulphite are liable to change more or less quickly, and it is often necessary to determine their strength by some rapid and simple manner. The methods employed for standardising hydrosulphite solution for use in *Indigo Analysis* (see p. 820) may be employed, though there is great risk of oxidising the sample in diluting it to the strength necessary for this operation. Water used for this purpose should be well boiled and cooled out of contact with air. For practical purposes in the dyehouse it is better not to dilute the hydrosulphite solution, and it is quite unnecessary to use any elaborate apparatus for excluding air. The method recommended by the *Badische Anilin- und Soda-Fabrik* answers every requirement. An indigo solution is prepared by dissolving 2 grms. of indigotin in sulphuric acid and diluting to a litre; or, 4 grms. of Indigo carmine, containing 50 per cent. indigotin, may be dissolved direct in a litre of water. 250 c.c. of this solution are poured into a flask of about 500 c.c. capacity, and whilst giving the flask a constant swirling motion, the hydrosulphite solution is carefully, but not too slowly, run in from a drop-pipette (divided into tenths of a cubic centimetre) until the blue colour changes to pale yellow. The number of c.c. required multiplied by 2 gives the volume of hydrosulphite necessary to reduce 1 gm. of indigotin.

Of late years solid hydrosulphites have come largely into the market, and in order to avoid the loss, through decomposition and oxidation, which may take place in dissolving these compounds in water Knecht\* has worked out the following process:—

**Estimation by Methylene Blue and Titanous Chloride.**—The principle of the method consists in adding a weighed quantity of the hydrosulphite powder to an excess of a standardised solution of Methylene blue, contained in a flask through which a current of carbon dioxide is being passed. The hydrosulphite at once reduces its equivalent of Methylene blue, and the excess is determined by titration with titanous chloride. About 0.2 gm. of the hydrosulphite is added to 25 c.c. of a 1 per cent. solution of Methylene blue. Before titrating the excess with titanous chloride, the solution is acidified with acetic acid. For the preparation of the standard solution of titanous chloride ( $\text{TiCl}_3$ ) see under *Iron Compounds* (p. 793).

Instead of using Methylene blue and titanous chloride a weighed amount of the hydrosulphite powder may be added to an excess of standardised indigotin solution, and the excess determined by a standard solution of hydrosulphite as in the *Analysis of Indigo* (p. 820).

**Sodium Sulphoxylate-Formaldehyde**, known in commerce under the names of *Rongalite C*, *Hydraldite C Extra*, and *Hydrosulphite NF Extra*, may

\* *Journ. Soc. Dyers and Col.*, 1907, p. 286.

be examined by the same methods given above for sodium hydrosulphite, with this difference, that the operation must be conducted at the boil. The simplest plan is to make up a standard solution of Indigo carmine. A given quantity of this solution is run into a flask and acidulated with acetic acid. A current of carbon dioxide is passed through the flask and the liquid boiled. Whilst boiling it is slowly titrated with a solution of the sample of known strength until the blue colour is discharged.

**Analysis of Hydrogen Peroxide.**—Peroxide of hydrogen in solution is sold containing ten or twelve volumes of oxygen. This denotes that one volume of the liquid contains peroxide in such quantity as to evolve ten or twelve volumes of oxygen respectively when reduced to water. The value of a sample depends upon the amount of available oxygen present.

**Estimation by Iodine and Thiosulphate.**—Kingzett\* has shown that the best method of estimating peroxide of hydrogen is by means of iodine and thiosulphate. The peroxide in an acid solution liberates an equivalent of iodine from potassium iodide, which is thus estimated by  $\frac{N}{10}$  thiosulphate. About 10 c.c. of the sample are diluted with water to 100 c.c., and 10 c.c. of this solution, mixed with 30 c.c. of a mixture of equal volumes of water and sulphuric acid, and an excess of potassium iodide added. After standing about five minutes, the liberated iodine is titrated with  $\frac{N}{10}$  thiosulphate and starch, as described under chloride of lime (p. 783).

1 c.c. of  $\frac{N}{10}$  thiosulphate = 0.0017 grm. of  $H_2O_2$  or 0.0008 grm. of oxygen.  
1 grm. oxygen = 697.5 c.c. at 0° C.

**Estimation by Potassium Permanganate.**—In the absence of other bodies acted upon by permanganate, this forms a ready means of determining the value of hydrogen peroxide. A measured quantity of the sample (2 c.c. of 12 volumes strength is a convenient amount) is acidulated with sulphuric acid and  $\frac{N}{10}$  permanganate added until a faint pink colour appears.

1 c.c. of  $\frac{N}{10}$  permanganate = 0.0017 grm. of  $H_2O_2$ .

**Titration by Titanous Chloride.**—This method, which has been worked out by Knecht and Hibbert,† gives accurate results, and may be found useful in presence of oxidisable substances. It is based upon the observation that if a dilute solution of titanous chloride is added to a solution of hydrogen peroxide, the well-known intensely orange colouration due to the formation of  $TiO_3$  appears. Up to a certain point the intensity of the colour increases, and by further additions of the  $TiCl_3$  then decreases until it vanishes altogether. This point is coincident with the complete reduction of the  $H_2O_2$ .

10 c.c. of the sample are diluted to 250 c.c., and of this 10 c.c. are titrated with standardised  $TiCl_3$  solution until decolourised.

56 Fe = 17  $H_2O_2$

**Gasometric Determination.**—Coulamine‡ recommends the following process as a rapid means of estimating hydrogen peroxide:—10 to 20 c.c. are neutralised with ammonia and diluted to 250 c.c. 25 c.c. of this solution are introduced into a gas absorption tube graduated for 50 c.c. in  $\frac{1}{10}$  c.c., a few crystals of potassium permanganate wrapped in tissue paper are added, the tube quickly closed by the thumb and vigorously shaken. When the reaction is complete, the tube is inverted over water and the volume of gas evolved read off.

This method, however, is not very exact.

\* *Journ. Chem. Soc. (Tr.)*, 1880, p. 792.

† *Berl. Ber.*, 1905, p. 3324.

‡ *Journ. Soc. Dyers and Col.*, 1886 p. 7.

**Analysis of Sodium Peroxide.**—Sodium peroxide may be analysed by the same methods as those given for hydrogen peroxide.

R. Niemeier \* finds that, with care, the permanganate method gives trustworthy results. 0.15 to 0.2 gram. of the peroxide is weighed out in a little dish placed in a weighing tube. This is then seized with a pair of tongs and quickly immersed in a beaker containing 500 c.c. of water; care should be taken that none of the peroxide floats on the surface, as otherwise the experiment fails. A sufficiency of dilute sulphuric acid is now added, and the liquid titrated at once with  $\frac{N}{10}$  permanganate.

L. Archbutt† recommends the following process:—about 0.25 gram. of the sample is introduced into the dry tube of a nitrometer flask, and about 5 c.c. of water (containing a few milligrammes of precipitated cobalt sesquioxide in suspension), are placed in the flask itself.

Rapid and complete decomposition of the sodium peroxide results immediately it is brought into contact with water, and the volume of the oxygen evolved is the available oxygen contained in the weight of peroxide taken.

A sample of the commercial substance tested by the above method (except that a drop of cobalt nitrate was used instead of precipitated cobaltic oxide) gave in three experiments 18.54, 18.46, and 18.57 per cent. of available oxygen. The same sample contained 78.66 per cent. of sodium oxide, and 0.49 per cent. of alumina and iron oxide. Hence the calculated composition was:—

Sodium peroxide ( $\text{Na}_2\text{O}_2$ ), . . . . .	90.41 per cent.
Caustic soda ( $\text{NaOH}$ ), . . . . .	8.73 „
Alumina and oxide of iron, . . . . .	0.49 „
Undetermined, . . . . .	0.37 „

This sample contained a very little carbonate, a trace of chloride, a minute trace of sulphate, and a few particles of unoxidised metallic sodium. No other impurity was detected.

\* *Chem. Zeit.*, 1907, p. 1257; *Journ. Chem. Soc. (Abs.)*, 1908 (94), p. 132.

† *Analyst*, 1895, p. 3; *Journ. Soc. Dyers and Col.*, 1895, p. 141.

## ANALYSIS OF MORDANTS, FIXING AGENTS, &amp;c.

## ALUMINIUM COMPOUNDS.

**Analysis of Alum.**—The two principal varieties of aluminium alums are potash alum,  $\text{Al}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ , and ammonia alum,  $\text{Al}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ .

Potash alum contains 10.76 per cent. of alumina,  $\text{Al}_2\text{O}_3$ , and ammonia alum contains 11.27 per cent. Potash alum is rather more soluble than ammonia alum; 100 parts of water at 20° C. dissolve 15.1 parts of the former and 13.6 parts of the latter. In other respects, so far as the dyer is concerned, they may be considered as identical.

Ammonia alum is readily distinguished from potash alum by evolving ammonia when boiled with caustic soda.

**Impurities.**—Alum in the crystallised state cannot well be adulterated, but iron and free sulphuric acid may be present as impurities.

Iron may be readily detected by adding a mixture of potassium ferro- and ferricyanides, which quickly produce a blue colour with iron. A greyish-blue colour is *gradually* developed with *pure* alum. Tannic acid may also be used as a test for iron, with which it gives a grey or black colouration. The amount of iron present is best determined colorimetrically as on p. 770 under water.

**Free Sulphuric Acid.**—For the detection of free acid in alums and aluminium sulphate, Watson Smith\* recommends the use of ferric acetate, the red colour of which is destroyed by a trace of free acid. The operation is best performed in a porcelain dish. Congo-red, a colouring matter which turns blue with free acids, has been recommended for the same purpose, also Methyl violet, which likewise turns blue with traces of free acid.

A preferable method (and one which admits of a ready quantitative determination) is to treat the powdered sample with strong alcohol containing a little phenolphthalein and rendered pink with addition of potash. If free sulphuric acid be present the colour is removed, and by titrating the filtered solution with  $\frac{N}{10}$  alkali the amount present is readily ascertained.

Alum purchased in the ground state may contain a variety of substances—such as common salt, sodium sulphate, and excess of water. The best method of ascertaining the value of such samples is to determine the amount of alumina by precipitation with ammonia. 1 grm. is weighed out and dissolved in about 200 c.c. of water, a considerable amount of ammonium chloride is added and a *slight* excess of ammonium hydrate. The liquid is kept near the boiling point for some time until the smell of ammonia disappears, when it is filtered and the precipitate well washed with boiling water. The precipitate is dried and ignited in a crucible and weighed as  $\text{Al}_2\text{O}_3$ .

**Analysis of Aluminium Sulphate** (*Cake Alum, Concentrated Alum, Patent Alum*)—It contains in a pure state 15 per cent. of alumina, and may be examined in exactly the same manner as alum.

For detecting and estimating free sulphuric acid in aluminium sulphate Beilstein and Grosset† recommend the following process:—1 to 2 grms. are dissolved in 5 c.c. of water and 5 c.c. of a cold saturated solution of ammonium sulphate added. After a quarter of an hour 50 c.c. of 95 per cent. alcohol are added, and the whole filtered and washed with 50 c.c. of the same liquid. The alcoholic liquor may then be examined for free acid as in alum.

\* *Journ. Soc. Dyers and Col.*, 1884, p. 35.

† *Journ. Soc. Chem. Ind.*, 1890, p. 416.

Aluminium sulphate crystallises with difficulty, and is more liable to contain impurities than alum. In many cases it is considered by dyers not to give such good results as common alum; this may probably be due to irregular composition and to the absence of sulphate of potash or ammonia. Iron may be detected and estimated as in alum.

Aluminium sulphate is largely used in the manufacture of other aluminium mordants.

**Analysis of Aluminium Acetate** (*Red Liquor, Red Mordant, Pyrolignite of Alumina*).—It is usually sold at a strength of about 24° Tw., and may be prepared by the action of aluminium sulphate upon lead or calcium acetate. The best method of examining samples of red liquor is by means of comparative dye-tests. For this purpose equal weights of cotton are impregnated with equal quantities of the samples to be examined in the same manner as described under *Application of Aluminium Mordants* (p. 234), and subsequently dyed with Alizarin or some other mordant-colour. The dyed material is then dried, and the swatches compared.

**Estimation of Alumina**.—About 5 grms. of the sample are evaporated to dryness in a platinum dish, and the residue gently ignited to destroy organic matter. When cold, the residue is dissolved in hydrochloric acid, and the alumina precipitated by ammonia, as described under *Alum*.

**Estimation of Acetic Acid**.—This is best performed by distillation with phosphoric acid, and titration of the distillate with normal caustic soda and phenolphthalein, as described under *Calcium Acetate* (p. 764).

**Analysis of Sodium Aluminate**.—On adding an acid to a solution of sodium aluminate with phenolphthalein as indicator, the neutral point is reached when all the alkali has been saturated. With methyl orange as indicator the end reaction occurs only when sufficient acid has been added to form the normal aluminium salt,  $\text{Al}_2(\text{SO}_4)_3$ . Lunge's method\* of analysis is based on these reactions:—20 grms. of sodium aluminate are dissolved in a litre, and 10 c.c. titrated hot with  $\frac{N}{2}$  hydrochloric acid in the presence of phenolphthalein until the red colour just disappears. The number of c.c. are read off, and after adding methyl orange the titration of acid is continued until the solution becomes faintly red. The first number corresponds with the soda present and the additional amount of acid used gives the alumina.

1 c.c.  $\frac{N}{2}$  HCl = 0.0062 grm.  $\text{Na}_2\text{O}$  and 0.0034 grm.  $\text{Al}_2\text{O}_3$ .

## CHROMIUM COMPOUNDS.

**Analysis of Bichromates**.—The most important chromium mordants are potassium and sodium bichromates.

Potassium bichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , known to the trade also as "*bichrome,*" or "*chrome,*" in the crystallised state is usually nearly pure, although samples have been found to contain a considerable amount of potassium sulphate. This was probably due to imperfect manufacture, since the potassium sulphate so found had evidently been present in the liquor during crystallisation.

100 parts of water at 15° C. dissolve 10 parts of potassium bichromate. It crystallises without water, and contains 68.09 per cent. of  $\text{CrO}_3$ . Sodium bichromate is a very deliquescent salt, and is very soluble in water. 100 parts of water at 15° C. dissolve about 110 parts of the anhydrous salt.

Sodium bichromate has now in a great many instances displaced the more expensive potassium salt. There are two chief varieties of commercial sodium bichromate—viz., the crystalline and the amorphous or lump. Crystallised sodium bichromate,  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , contains nearly the same

\* *Zeits. für angew. Chem.*, 1890, p. 293; *Journ. Soc. Chem. Ind.*, 1890, p. 767.

amount of chromic acid as potassium bichromate—viz., 67·70 per cent. The dry lump also usually contains about the same amount (some more, others less): but in place of water of crystallisation it contains sodium sulphate and other impurities. The crude varieties of sodium bichromate often contain considerable quantities of normal chromate, which is a much less effective mordant than the acid salt.

**Estimation of Chromic Acid.**—The usual method of estimating chromic acid in chromates and bichromates consists in adding an excess of ferrous ammonium sulphate to an acidulated solution of the sample and titrating the residual ferrous salt with decinormal potassium bichromate. In lieu of this mode of procedure the following plan can be recommended:—Weigh out 5 grms. of the sample and dissolve in a litre of water, with which solution fill a burette. In the case of sodium bichromate, in order to obtain a fair average sample, it is preferable to weigh out 25 grms. and dissolve in 500 c.c., and then, after shaking, take out 100 c.c. and dilute to a litre. 1 gm. of pure granulated ferrous ammonium sulphate is then weighed out and dissolved in a little water in a porcelain basin and 50 c.c. of a 10 per cent. solution of sulphuric acid added. The solution of bichromate is then added during constant stirring with a glass rod until a drop of the liquid ceases to give a blue or greenish-blue colouration when brought in contact with a drop of potassium ferricyanide solution on a porcelain slab. 1 gm. of ferrous ammonium sulphate reduces 0·0854 gm. of  $\text{CrO}_3$ ; consequently, the number of c.c. of the solution required contains this amount of chromic acid.

*Example.*—5 grms. of potassium bichromate were dissolved in a litre of water. Of this solution, 1 gm. of ferrous ammonium sulphate required 25·2 c.c.

$$\therefore 25\cdot2 \text{ c.c.} = 0\cdot0854 \text{ gm. of } \text{CrO}_3$$

$$\therefore 1000 \text{ c.c.} = 3\cdot388 \text{ grms. of } \text{CrO}_3$$

$$\frac{3\cdot388 \times 100}{5} = 67\cdot76 \text{ per cent. of } \text{CrO}_3.$$

Chromic acid may be determined *gravimetrically* by conversion either into chromic oxide or chromate of lead. The former process is carried out by dissolving 0·5 gm. of the sample of bichromate (or by taking 100 c.c. of the solution above mentioned) in a little water, adding hydrochloric acid, and heating either with alcohol or sulphurous acid. The excess of alcohol or sulphurous acid is boiled off and the green solution diluted to about 200 c.c. treated with a *slight* excess of ammonia. The precipitate is collected on a filter, well washed, dried, ignited, and weighed as  $\text{Cr}_2\text{O}_3$ . 153 parts of  $\text{Cr}_2\text{O}_3$  correspond to 201 parts of  $\text{CrO}_3$ .

**Estimation of Normal Chromate.**—Potassium bichromate rarely contains normal chromate, but, as previously stated the sodium compound frequently contains considerable quantities. At the present time, however, it is not so prevalent as it was a few years ago. Three methods for estimating normal chromate will be described, but, when present in small quantities preference is given to the first process.

1. M'Culloch's process\* depends upon the fact that free chromic acid, when shaken up with peroxide of hydrogen and ether, imparts a blue colouration to the ether; whereas neither chromate nor bichromate produces any effect. If bichromate alone is taken, a drop or two of acid is sufficient to produce the blue colour, whereas, if normal chromate is present, acid must be added in sufficient quantity to convert it into bichromate. The following plan of carrying out the operation is recommended:—2·5 to 5 grms. of the sample are dissolved in 40 to 50 c.c. of water, and the solution introduced into a stoppered

\* *Chem. News*, vol. lv. (1887), p. 2.

cylinder, holding about 120 c.c. 10 c.c. of hydrogen peroxide (10 vols.) and about 20 c.c. of ether are added and the contents shaken. (If free chromic acid be present the ethereal layer will be of a blue colour.) A decinormal solution of sulphuric acid is now added in small quantities at a time with frequent agitation until the ether is tinged faintly blue, which is best seen against a white background. Each c.c. of  $\frac{N}{10}$  acid corresponds to 0.01005 grm. of  $\text{CrO}_3$  as normal chromate = 0.01625 grm. of  $\text{Na}_2\text{CrO}_4$  or 0.01945 grm. of  $\text{K}_2\text{CrO}_4$ .

If the hydrogen peroxide contains acid, this must be taken into account.

2. In the paper above mentioned, M'Culloch refers to the direct determination of bichromate by means of standard soda and phenolphthalein, and thence by deducting chromic acid so found from the total chromic acid, calculating the amount of normal chromate present. He correctly points out that the end reaction is not sharp and precise, but if an excess of caustic soda be added and the liquid titrated back with standard acid this difficulty is altogether overcome.

1 c.c. of  $\frac{N}{10}$  soda = 0.01005 grm. of  $\text{CrO}_3$  as bichromate.

3. R. T. Thomson\* has shown that bichromate of potash or soda is neutral to lackmoid, whilst normal chromate is alkaline. Normal chromate may, therefore, be estimated in bichromate by standard acid and lackmoid paper. Free chromic acid may be likewise determined by using decinormal soda.

*Examples.*—A sample of impure bichromate of soda gave 70.60 per cent. of total chromic acid,  $\text{CrO}_3$ .

*By Method 1.*—2.5 grms. with hydrogen peroxide and ether required 30.6 c.c. of  $\frac{N}{10}$  sulphuric acid.

$$\therefore \frac{0.01005 \times 30.6 \times 100}{2.5} = 12.30 \text{ per cent. of } \text{CrO}_3 \text{ as chromate,}$$

$$\therefore \text{by difference} = 58.30 \text{ per cent. of } \text{CrO}_3 \text{ as bichromate.}$$

*By Method 2.*—50 c.c. of a 1 per cent. solution (= 0.5 grm.) were treated with a few drops of phenolphthalein and 35 c.c. of  $\frac{N}{10}$  caustic soda. 6.1 c.c. of  $\frac{N}{10}$  acid were then required to produce a pure yellow solution.

$$\therefore \frac{0.01005 \times 28.9 \times 100}{0.5} = 58.08 \text{ per cent. of } \text{CrO}_3 \text{ as bichromate,}$$

$$\text{and by difference} = 12.52 \text{ per cent. of } \text{CrO}_3 \text{ as chromate.}$$

*By Method 3.*—100 c.c. of a 1 per cent. solution (= 1 grm.) were titrated with  $\frac{N}{10}$  sulphuric acid, using lackmoid paper as an indicator. 12.6 c.c. were required.

$$\therefore 0.01005 \times 12.6 \times 100 = 12.66 \text{ per cent. of } \text{CrO}_3 \text{ as chromate,}$$

$$\text{and by difference} = 57.94 \text{ per cent. of } \text{CrO}_3 \text{ as bichromate.}$$

Sulphuric Acid as potassium or sodium sulphate in bichromates may be directly determined by precipitation with barium chloride in a dilute and acid solution, but more accurate results are obtained by previously reducing the chromic acid to chromic oxide by means of alcohol and hydrochloric acid.

**Chrome Alum** possesses a similar constitution to common alum—viz.,  $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ . It is liable to contain tarry organic matter, calcium sulphate, and sodium sulphate as impurities. The chromium oxide may be determined by precipitation with ammonia as alumina in common alum.

**Chromium Acetate** is usually sold in solution at 30° to 36° Tw. containing about 15 to 17 per cent. of chromium acetate. It may be examined in precisely the same manner as aluminium acetate (p. 789).

\* *Chem. News*, vol. lii. (1885), p. 29.



## IRON COMPOUNDS.

**Analysis of Ferrous Sulphate.**—This salt, known also as *copperas* and *green vitriol*, crystallises with seven molecules of water. It was formerly largely used in conjunction with logwood for dyeing blacks upon wool, but has been almost entirely replaced by bichromates. It is now used principally in cotton dyeing. Exposed to moist air, ferrous sulphate becomes covered with a brown film of basic ferric sulphate. For some purposes this is considered rather advantageous than otherwise, but if used for *vat indigo dyeing* the ferric sulphate is merely so much waste material.

*Ferrous iron* is readily estimated, either by a standard solution of bichromate or of permanganate. The estimation by bichromate is merely the reverse of the method already described for *Chromic Acid* (p. 790). The estimation by permanganate is carried out as follows:—

**Preparation of Decinormal Permanganate Solution.**—3.156 grms. of pure dry potassium permanganate are dissolved in a litre of distilled water. The solution requires standardising, since perfectly pure potassium permanganate is not easily obtainable. This is most readily performed by means of pure granulated ferrous ammonium sulphate. 0.7 gm. of this salt (=0.1 gm. of iron) is dissolved in about 100 c.c. of water in a porcelain basin, and 50 c.c. of a 10 per cent. solution of sulphuric acid added. The permanganate solution is now gradually run in from a burette, with constant stirring, until the liquid becomes a faint pink colour. If strictly decinormal, 17.85 c.c. will be required.

Instead of taking ferrous ammonium sulphate, the permanganate may also be standardised by means of pure clean iron wire. 0.1 gm. is introduced into a small flask fitted with a bent glass tube and Bunsen's valve (see below, *Estimation of Total Iron*), and dissolved in dilute sulphuric acid. When dissolved, the liquid is allowed to cool, and titrated with the permanganate solution, as above described.

*Ferrous ammonium sulphate*, a salt frequently mentioned in this division, has a composition represented by the formula  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and contains exactly one-seventh of its weight of iron. It is prepared by mixing equivalent proportions of pure ferrous sulphate and ammonium sulphate (dissolved separately), and allowing the double salt to crystallise out. It occurs in commerce in crystals and in a fine granulated form. For use in chemical analysis, the latter is to be preferred. It should be preserved in a well-stoppered bottle. If there is any doubt about its purity, a weighed amount should be dissolved in water, with addition of a little sulphuric acid; the solution oxidised by nitric acid, and the iron estimated gravimetrically (see *Analysis of Ferric Sulphate*). Another portion should be dissolved in a little water, and tested for *ferric iron* by means of potassium thiocyanate.

**Estimation of Ferrous Oxide.**—1 gm. of the sample of ferrous sulphate (or 100 c.c. of a 1 per cent. solution) is dissolved in about 100 c.c. of water and 50 c.c. of a 10 per cent. solution of sulphuric acid added. The solution is then titrated in a porcelain dish with  $\frac{N}{10}$  potassium permanganate until a faint pink colour remains for about half a minute after stirring. 1 c.c. of  $\frac{N}{10}$  permanganate = 0.0072 gm. of FeO or 0.0278 gm. of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

**Estimation of Total Iron.**—1 gm. is washed into a small flask with about 50 c.c. of water; 5 to 10 c.c. of strong sulphuric acid and a rod of zinc free from iron are then introduced. The flask is fitted with a cork and bent glass tube, to which is attached a Bunsen's valve. This merely consists of a short piece of india-rubber tubing closed at one end with a glass rod and having a longitudinal slit in the centre. Steam and hydrogen can by this arrangement easily escape from the flask, but air is unable to enter. The flask is inclined at

an angle of about  $45^\circ$  and gently heated. When the reduction is complete (known by a drop of the liquid producing no colouration with a drop of potassium thiocyanate) recently boiled and cooled water is allowed to enter the flask, and the liquid titrated with  $\frac{N}{10}$  permanganate as above. If the rod of zinc has not thoroughly dissolved, it must be carefully removed and washed before titrating with permanganate. The difference between this titration and the direct titration represents the amount of iron present in the ferric state. 1 c.c. of  $\frac{N}{10}$  permanganate = 0.008 grm. of  $\text{Fe}_2\text{O}_3$ .

**Estimation of Iron by Titanous Chloride.**—Knecht and Hibbert\* estimate iron by titanous chloride as follows:—50 c.c. of 20 per cent. titanous chloride and 50 c.c. of strong hydrochloric acid are boiled together, cooled, and made up to about 2 litres. With a powerful reducing agent like titanous chloride it is not astonishing that it should rapidly absorb oxygen from the air, and it is therefore absolutely necessary, if reliable results are to be obtained, that it should be stored and measured in vessels in which it is out of contact with the air. A simple arrangement for this purpose is shown in Fig. 118. Sufficient of the reagent is prepared to completely fill the storage vessel S, which is connected with the burette B, both storage vessel and burette being kept under constant hydrogen pressure from the small hydrogen generator G, where the gas is produced from zinc and hydrochloric acid. When liquid is withdrawn from the burette at P, the pressure is released and hydrogen is at once generated at G, so that the interior of the apparatus, which is not filled with liquid, contains hydrogen at a pressure of about 3 inches.

The reaction on which this method is based takes place according to the equation:  $\text{TiCl}_3 + \text{FeCl}_3 = \text{TiCl}_4 + \text{FeCl}_2$ .

The solution is standardised by means of pure ferrous ammonium sulphate. 0.35 grm. of this salt is dissolved in a little water, acidified and titrated with potassium permanganate until faintly pink. The oxidised iron solution, to which an excess of potassium sulphocyanide has been added, is now titrated with the solution of titanous chloride to be standardised until the red colouration disappears. The number of c.c. required divided into 0.05 will give amount of iron equivalent to each c.c. of the standard solution.

The estimation of ferric iron in a compound is carried out in exactly the same way as in standardising. Ferrous iron must first be oxidised to ferric by any well known means.

**Estimation of Iron by Hydrosulphite.**—In his original paper on the analysis of indigo, Rawson † pointed out that ferric iron was reduced quantitatively to ferrous iron by sodium hydrosulphite. The operation is carried out in an acid solution, without access of air, and with indigo carmine as indicator, exactly as in standardising sodium hydrosulphite solution by means of ammoniacal copper sulphate. (See *Analysis of Indigo, hydrosulphite method*, p. 820). One molecule of ferric sulphate requires the same amount of hydrosulphite for reduction as one molecule of copper sulphate.

Alumina may be detected in ferrous sulphate by boiling with addition of sulphuric and nitric acids to oxidise the iron, and adding an excess of pure caustic soda. The liquid is boiled and filtered, and to the filtrate hydrochloric acid and ammonia added, when, if alumina be present, a white gelatinous

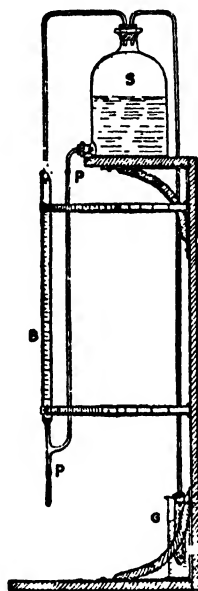


Fig. 118.

\* *Berl. Ber.*, 1903, p. 1549.

† *Journ. Soc. Dyers and Col.*, 1885, p. 77.

precipitate will be obtained. The latter may be filtered off, washed, dried, ignited, and weighed as  $\text{Al}_2\text{O}_3$ .

**Acetate of Iron** is sold in solution under the names of *iron liquor*, *black liquor*, and *pyrolignite of iron*.

The best practical method of ascertaining the value of acetate of iron is to make careful dye-trials, as with ferric sulphate. The total amount of *iron* and *acetic acid* present may be determined in the same manner as alumina and acetic acid in aluminium acetate (p. 789). The iron may also be determined by igniting to destroy organic matter; dissolving the residue in hydrochloric acid, reducing with zinc and titrating the solution with permanganate.

**Impurities.**—Commercial acetate of iron may contain ferrous sulphate, ferrous chloride, sodium sulphate, and sodium chloride. Sodium salts may be detected and estimated by adding an excess of ammonia and evaporating the filtrate to dryness, and igniting. The amount of ferrous sulphate or ferrous chloride, in the absence of alkaline salts, may be determined by estimating the sulphuric or hydrochloric acid present.

**Analysis of Ferric Sulphate.**—Solutions of ferric sulphate, more or less basic, with and without ferrous sulphate, are largely used in cotton and silk dyeing under the name of *Nitrate of iron*.

The solutions usually have a strength of about 80° Tw., and contain about 10 per cent. of iron.

If ferrous sulphate is present a blue precipitate will be obtained with potassium ferricyanide.

**Estimation of Total Iron**—25 c.c. (measured in a specific gravity bottle, and weighed) are diluted to 500 c.c. 25 c.c. are withdrawn and diluted to about 200 c.c. If any iron is present in the ferrous state, it is preferable to add a few drops of nitric acid, and boil for some minutes. A slight excess of ammonia is added, and the liquid filtered. The precipitate should be washed two or three times with hot water by decantation before bringing it wholly on to the filter. The precipitate may be either dried, ignited, and weighed as  $\text{Fe}_2\text{O}_3$  or dissolved in sulphuric acid, reduced by zinc, and titrated with  $\frac{N}{10}$  permanganate, as given under ferrous sulphate; or, the ferric sulphate solution may be titrated directly by titanous chloride.

In the absence of nitric acid or nitrates, the 25 c.c. of the diluted solution may be reduced direct, and titrated with permanganate.

1 c.c. of  $\frac{N}{10}$  permanganate = 0.0056 grm. of Fe.

**Estimation of Ferrous Iron.**—5 to 10 c.c. of the sample are weighed, diluted with water, and acidulated with sulphuric acid. The solution is then titrated with  $\frac{N}{10}$  permanganate.

1 c.c. = 0.0056 grm. of Fe, or 0.0072 grm. of  $\text{FeO}$ .

The amount of ferric oxide is obtained by deducting ferrous iron from the total and calculating into  $\text{Fe}_2\text{O}_3$ .

**Sulphuric acid** is best determined by acidulating the filtrate from the ferric oxide precipitate with hydrochloric acid, and adding barium chloride. If barium chloride is added direct to the ferric sulphate solution the barium sulphate is liable to be contaminated with iron.

**Hydrochloric acid** should also be determined, after removal of the oxide of iron by ammonia, by acidulating the solution with nitric acid and adding silver nitrate.

**Sodium salts** may be detected and estimated by adding ammonia, and evaporating the filtrate to dryness, and igniting the residue. If iron compounds only were present nothing more than a trace would remain after ignition.

**Relation of Acid to Base.**—In the analysis of ferric sulphate one of the most important matters is to determine the relative proportion of total acid and ferric oxides present. For most purposes, commercial “nitrate of iron” or ferric sulphate should contain less acid than that necessary to form normal ferric sulphate. Some samples contain a slight excess of acid. The amount of acid in combination with iron (as well as any free acid, if present) is best determined by taking 2 to 5 grms. of the sample, diluting with about 200 c.c. of water, and adding a slight excess of normal solution of sodium carbonate. The liquid is boiled and filtered, and the precipitate well washed with hot water. The excess of sodium carbonate is then estimated by normal sulphuric acid and methyl orange. Each c.c. of normal sodium carbonate = 0.040 gm. of  $\text{SO}_3$ .

*Example.*—2.5 c.c. = 3.56 grms. of ferric sulphate were treated with 22 c.c. of normal  $\text{Na}_2\text{CO}_3$ . The filtrate required 4 c.c. of normal  $\text{H}_2\text{SO}_4$ .

$$\therefore \frac{0.040 \times 18 \times 100}{3.56} = 20.22 \text{ per cent. of } \text{SO}_3, \text{ combined with ferric and ferrous oxides.}$$

The amount of  $\text{SO}_3$  required to combine with the found percentages of ferric and ferrous oxides to form normal sulphates is calculated and compared with the actual amount of acid present. Instead of using sodium carbonate, boiling and filtering as above given, fairly good results may be obtained by titrating direct with normal caustic soda and phenolphthalein, as in the case of tin mordants (p. 796); but the end reaction is not very distinct.

The following figures show the results of analysis of a few samples of average ferric sulphate or “nitrate of iron” :—

	1.	2.	3.	4.
Specific gravity, . . . . .	1.410	1.402	1.405	1.345
Equal to degrees Twaddle, . . . . .	82°	80°	81°	69°
Total iron, . . . . .	11.80	10.88	10.97	9.59
Ferric oxide, . . . . .	16.86	15.45	12.00	12.72
Ferrous oxide, . . . . .	none	.15	3.32	.86
Sulphuric acid ( $\text{SO}_3$ ), . . . . .	16.61	17.20	16.75	16.20
Hydrochloric acid (HCl), . . . . .	1.64	.06	...	...
Total acid combined with iron in terms of $\text{SO}_3$ , . . . . .	20.05	17.30	16.96	16.40
Calculated $\text{SO}_3$ required to form normal sulphates, . . . . .	25.30	23.39	22.74	20.31

“Nitrate of iron” should always be tested practically by experimental dye-trials. If intended for cotton dyeing the following plan might be adopted :—Swatches of calico or cotton yarn, each weighing 10 grms., are thoroughly wetted out and worked together for about an hour in a decoction of sumach or myrabolans. The swatches are taken out, the excess of liquid removed by shaking, and each piece put into a dilute solution (5 c.c. to 250 c.c.) of the sample of “nitrate of iron” to be examined. After 20 to 30 minutes the pieces are taken out, well washed, dried, and compared.

## TIN COMPOUNDS.

**Analysis of Stannous Chloride.**—This salt crystallises with 2 molecules of water,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . It is commonly known in the dye-house as *tin crystals*.

Stannous chloride is occasionally found adulterated with zinc or magnesium sulphates or zinc chloride.

*Sulphates* may be readily detected by addition of hydrochloric acid and barium chloride.

*Zinc* and *magnesia* may be detected in the filtrate after precipitating the tin as sulphide by a current of sulphuretted hydrogen in an acid solution.

**Estimation of T.N.**—About 0.25 grm. of the sample is dissolved in a little water containing hydrochloric acid, and mixed with 50 c.c. of a 10 per cent. solution of Rochelle salt (potassium-sodium tartrate) and 50 c.c. of a 10 per cent. solution of sodium bicarbonate. A little starch solution is then added and the liquid titrated with  $\frac{N}{10}$  iodine until a permanent blue colour appears.

1 c.c. of  $\frac{N}{10}$  iodine = 0.0059 grm. of Sn.

Fairly good results may also be obtained by simply dissolving the "tin crystals" in dilute hydrochloric acid and titrating direct with  $\frac{N}{10}$  iodine without starch.

**Indirect Estimation by Permanganate.**—0.5 grm. is dissolved in water and hydrochloric acid. A slight excess of ferric chloride is then added, which oxidises the tin to stannic chloride, becoming itself reduced to ferrous chloride. The liquid is diluted with recently boiled and cooled water and titrated with  $\frac{N}{10}$  potassium permanganate, each c.c. of which corresponds to 0.0059 grm. of Sn.

**Estimation by Titanous Chloride.**—Knecht and Hibbert\* add an excess of a standard solution of iron alum to the stannous chloride solution. The liquid is heated to the boil whilst a current of carbon dioxide is passed through. After cooling, the excess of iron alum is determined by titrating with standard titanous chloride.

**Solutions of Stannous Chloride**, containing hydrochloric acid, are sold under the names of *double muriate of tin* and *single muriate of tin, tin spirits*, &c. (see p. 273). The terms "double" and "single" merely refer to the density of the solutions. Single muriate varies in density from 40° to 60° Tw., and double muriate from 70° to 120° Tw. The same impurities (as well as free sulphuric acid) may be present as in tin crystals.

**Estimation of Stannous Chloride.**—The amount of tin present as stannous chloride may be estimated either by  $\frac{N}{10}$  iodine or by ferric chloride and  $\frac{N}{10}$  permanganate, as described above.

If *stannic chloride* is also present, which is frequently the case, the total amount of tin is estimated by allowing a piece of pure metallic zinc to remain in a weighed portion of the sample for 10 or 12 hours. If 25 c.c. of the sample are diluted to 500 c.c., 25 c.c. of this solution will be a convenient amount to take. The tin which is thus entirely precipitated in the metallic form, is carefully collected and washed, and dissolved in hydrochloric acid with the aid of platinum foil. This should be done in a flask in a current of carbon dioxide to prevent oxidation. The stannous chloride solution obtained is then titrated as above.

**Estimation of Free Acid.**—Since stannous chloride has an acid reaction to indicators, the free hydrochloric acid present cannot be titrated direct. In order to ascertain the amount of free acid present, it is necessary to determine the total acid (free and combined) and to calculate the amount required to

\* *Journ. Soc. Dyers and Col.*, 1905, p. 345.

combine with the percentage of tin found. For this purpose W. Minor\* recommends that 10 c.c. of the solution be diluted with water, and the tin precipitated as sulphide by a current of hydrogen sulphide. The filtrate is made up to a litre and 500 c.c. boiled, to expel  $H_2S$ , and titrated with a solution of soda. It is quite unnecessary, however, to separate the tin. The total acid may be accurately estimated by titrating the solution of stannous chloride direct with caustic soda and phenolphthalein. The stannous hydrate formed has no action whatever upon the indicator. If pure stannous chloride is titrated in this way, the exact amount of combined acid is obtained.

*Example.*—25 c.c. of a solution of single muriate of tin = 30.88 grms. were diluted to 500 c.c.

25 c.c. required 21.8 c.c. of  $\frac{N}{10}$  iodine = 8.33 per cent. of Sn.

50 c.c. of diluted solution (= 3.088 sample) with phenolphthalein required 19.8 c.c. of normal caustic soda.

1 c.c. normal soda = 0.0365 grm. of HCl.

$$\therefore \frac{0.0365 \times 19.8 \times 100}{3.088} = 23.40 \text{ per cent. of HCl free and combined.}$$

8.33 parts of Sn require 5.15 parts of HCl to form  $SnCl_2$ .

$$\therefore 23.40 - 5.15 = 18.25 \text{ per cent. of free HCl.}$$

**Analysis of Stannic Chloride.**—Solutions of stannic chloride are used under various names, consisting of stannic chloride only, and of mixtures of this salt with stannous chloride (see p 274). Acids other than hydrochloric acid, such as sulphuric, nitric, and oxalic, are also occasionally present. The liquid known as *solution of tin*, sold at about 44° Tw., and containing about 8 per cent. of tin, usually consists of stannic chloride only, with a slight excess of hydrochloric acid and a little nitric acid. If any *stannous* chloride is present, a drop of the liquid will produce a white or grey precipitate with a solution of mercuric chloride.

**Estimation of Tin.**—The amount of tin may be determined by precipitation with zinc, as already described; or by the following gravimetric process, which gives very accurate results:—About 5 grms. of the solution are diluted with water to 200 c.c., and, if any stannous salt be present, a weak solution of iodine is added until the liquid is faintly yellow. A dilute solution of ammonia is now gradually added until a faint opalescence appears, when an excess of a concentrated solution of sodium sulphate is added. The liquid is kept hot on the water-bath for one or two hours, and the somewhat voluminous precipitate washed two or three times by decantation. It is then collected on a filter, thoroughly washed, dried, ignited, and weighed as  $SnO_2$ .

$$150 \text{ parts of } SnO_2 = 118 \text{ parts of Sn.}$$

Free Acid in solutions of stannic chloride may be estimated by caustic soda and phenolphthalein, exactly in the same way as in solutions of stannous chloride. In calculating the combined acid four equivalents of hydrochloric acid must be taken in place of two.

P. Heermann, in his *Dyers' Materials* (English edition, p. 35), states that this method "is quite inaccurate and useless." In consequence of this statement, one of the authors has again investigated the matter and finds the adverse criticism to be entirely unfounded. Various known amounts of hydrochloric acid were added to stannic and stannous chlorides respectively, and, in every case, the exact amount of acid was found by direct titration as given above and as given in the first edition of this work.

In addition to being analysed, tin compounds should always be examined by experimental dye-trials. The exact mode of procedure would depend upon the purpose to which the mordant was to be applied on the large scale.

\* *Chem. News*, vol. lxiii. (1891), p. 249, from *Zeitsch. angew. Chemie*.

## TITANIUM COMPOUNDS.

**Analysis of Titanous Chloride.**—Titanous chloride is sold as a violet-coloured solution, containing about 20 per cent.  $TiCl_3$ . It is estimated by the method used in standardising titanous chloride solution for the determination of iron (p. 793). 5 c.c. of the sample are weighed out, mixed with 5 c.c. of strong hydrochloric acid, and made up with water to 100 c.c. 5 c.c. of this solution are withdrawn and titrated with standard iron alum solution, using potassium sulphocyanide as indicator.

**Titanous Sulphate** may be estimated in the same manner.

**Titanic Salts.**—The most rapid method of estimating the titanium in these is to reduce first with hydrochloric acid and zinc, and then titrate the titanous chloride formed either with iron alum or with standardised Methylene blue.

## COPPER COMPOUNDS.

**Analysis of Copper Sulphate.**—Copper sulphate, known also as *blue vitriol* and *blue stone*, crystallises with five molecules of water,  $CuSO_4 \cdot 5H_2O$ . It is liable to contain *ferrous sulphate* as an impurity. Commercial sulphate of copper invariably contains small quantities of iron.

**Estimation of Copper by Precipitation as  $CuO$ .**—0.5 gm. of the sample is dissolved in about 150 c.c. of water, in a porcelain basin, and heated to the boiling point. A slight excess of a solution of pure potassium or sodium hydrate is added, and the liquid gently boiled for about five minutes, when the brownish-black precipitate is allowed to subside, and the supernatant liquid poured through a small filter. Boiling water is added to the residue, and, after subsidence, the liquid is again poured off. This washing is repeated two or three times, when the whole of the precipitate is carefully transferred to the filter, and thoroughly washed with hot water. It is dried, transferred to a crucible, ignited, and weighed. The precipitate of oxide of copper should at first be ignited gently, but afterwards intensely, and weighed as soon as the crucible is cold. The ash of the filter should be ignited separately on the lid of the crucible, and any metallic copper contained therein converted into oxide by addition of a drop or two of nitric acid, and ignition. If iron is present in the sample, the precipitate will contain ferric oxide, which must be estimated and deducted (see below).

79.4 parts of copper oxide correspond to 63.4 parts of metallic copper or 249.4 parts of crystallised copper sulphate.

**Estimation by Precipitation as Metallic Copper.**—About 0.5 gm. of the sample is dissolved in a little water, in a weighed platinum dish. Sulphuric acid and a rod of pure zinc are added and the dish covered with a clock glass. The copper is thereby precipitated on the platinum. When the reaction is complete, known by a drop of the liquid producing no brown colour with sulphuretted hydrogen, the zinc is carefully removed, and the deposit thoroughly washed, dried at  $100^\circ C.$ , and weighed.

Instead of drying and weighing the metallic copper, it may be dissolved in a mixture of hydrochloric acid and ferric chloride (Fleitmann's method), diluted with water, and the ferrous chloride formed titrated with  $\frac{N}{10}$  permanganate.

**Estimation of Copper by Titanous Chloride.**—E. L. Rhead\* determines copper by means of titanous chloride in the presence of potassium thiocyanate. A small amount of ferrous ammonium sulphate is also added in order to ensure a sharp end reaction. The titration is carried out in the cold. The ferrous

\* *Intern. Chem. Soc. (Trans.)*, 1906, pp. 89, 1491; *Journ. Soc. Chem. Ind.*, 1906, p. 1175.

salt added is oxidised by the copper salt, and the end of the titration is indicated by the disappearance of the red colour due to ferric thiocyanate. In titrating 50 c.c. of a solution containing 2 grms. of copper sulphate per litre, 10 to 20 c.c. of a 10 per cent. solution of potassium thiocyanate are added. The titanous chloride solution is standardised by ferrous ammonium sulphate.

56 parts of iron = 63·5 parts of copper.

There are many other volumetric processes for estimating copper, descriptions of which may be found in Sutton's *Volumetric Analysis*.

**Estimation of Iron.**—About 5 grms. of the sample should be taken, dissolved in 100 c.c. of water and boiled with addition of a few drops of nitric acid. The liquid is cooled, diluted to about 300 c.c., and an excess of ammonium hydrate added. The ferric oxide which is thus precipitated is collected on a filter, washed, redissolved in hydrochloric acid, and again precipitated by ammonia in the cold. The liquid is filtered, the oxide of iron washed, dried, ignited, and weighed.

**Copper Acetate.**—Copper may be determined by igniting a weighed portion of the sample, dissolving in hydrochloric acid, and treating the solution as above.

*Acetic acid* is best estimated by distillation with phosphoric acid (see p. 764).

## ANTIMONY COMPOUNDS.

**Analysis of Tartar Emetic.**—This salt is largely used in cotton-dyeing and in calico-printing. It consists of the double tartrate of antimony and potassium, and contains half a molecule of water. Tartar emetic, especially if purchased in the powdered form, is liable to considerable adulteration; oxalate of antimony and the double fluoride of ammonium and antimony being most frequently used for this purpose.

Antimony as antimonious oxide may be readily estimated by titrating an alkaline solution with  $\frac{N}{10}$  iodine and starch. W. B. Hart's process,\* which consists in adding an excess of a solution of bleaching powder and titrating with  $\frac{N}{10}$  arsenious acid, can be recommended. 0·5 gm. of the sample is dissolved in about 50 c.c. of warm water and cooled. 20 c.c. of a 10 per cent. solution of sodium bicarbonate and 25 c.c. of a 2 per cent. solution of bleaching powder are added, and the liquid well stirred with a glass rod. If sufficient bleaching powder has been added, a drop of the liquid will now produce a blue colour with potassium iodide and starch paper. Decinormal sodium arsenite (4·95 grms. of  $\text{As}_2\text{O}_3$  per litre) is then run in until a drop of the liquid ceases to give any colouration with the iodide and starch paper (see p. 783). The strength of the bleaching-powder solution used to oxidise the antimony is determined, when the amount of chlorine expressed in terms of arsenite is readily calculated. 1 c.c. of  $\frac{N}{10}$  arsenite = 0·006 gm. of Sb or 0·0072 gm. of  $\text{Sb}_2\text{O}_3$ .

*Example.*—0·5 gm. of tartar emetic with sodium bicarbonate and 25 c.c. of chloride of lime required 7·5 c.c. of  $\frac{N}{10}$  arsenite 25 c.c. of chloride of lime alone required 36·5 c.c. of  $\frac{N}{10}$  arsenite. Therefore, chlorine equivalent to 29 c.c. of arsenite was used in oxidising the antimonious oxide present.

$$\therefore \frac{0\cdot0072 \times 29 \times 100}{0\cdot5} = 41\cdot76 \text{ per cent. of } \text{Sb}_2\text{O}_3.$$

Antimony may also be accurately estimated by precipitating it as  $\text{Sb}_2\text{S}_3$ , and (with due precautions regarding the presence of free sulphur) weighing it as such, or distilling the sulphide in a flask with hydrochloric acid, and collecting the hydrogen sulphide evolved in a known volume of  $\frac{N}{10}$  arsenite solution and estimating the excess of arsenite with thiosulphate (*Schneider*).

\* *Journ. Soc. Chem. Ind.*, 1884, p. 204.



Pure tartar emetic contains 43·4 per cent. of  $\text{Sb}_2\text{O}_5$ . Some samples in the market contain more than that amount, owing to the presence of ammonium antimony fluoride. If this salt is present, ammonia will be evolved on boiling with caustic soda.

Oxalate in tartar emetic may be detected and estimated, if necessary, by precipitating the antimony as sulphide in an acid solution. The filtrate is boiled to remove hydrogen sulphide, a slight excess of ammonia is then added, and the liquid made slightly acid with acetic acid, and treated with calcium chloride (see p. 766).

**Antimony Oxalate.**—The antimony in *oxalate of antimony* and other antimony salts may be determined as in tartar emetic. With salts containing antimony fluoride, however, Hurt's process does not give satisfactory results. In such cases it is preferable to titrate an alkaline solution of the salt with decinormal iodine.

### ARSENIC COMPOUNDS.

**Arsenious Acid** may be examined for percentage of  $\text{As}_2\text{O}_3$  by practically the same method as that described for standardising the  $\frac{N}{10}$  arsenite solution (p. 783). 2 grms. of the sample are dissolved in water containing about 5 grms. of sodium carbonate, and diluted to 500 c.c. 50 c.c. (= 0·2 gm.) are withdrawn, neutralised with a little pure hydrochloric acid, 25 c.c. of a saturated solution of sodium bicarbonate added, and the liquid titrated with  $\frac{N}{10}$  iodine.

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = 0\cdot00495 \text{ gm. } \text{As}_2\text{O}_3.$$

**Sodium Arsenate**,  $\text{Na}_2\text{HAsO}_4$ , is known as *dung salt* or *dung substitute*.

**Arsenious Acid**, if present, is estimated by titrating a weighed amount with  $\frac{N}{10}$  iodine, as above.

**Arsenic Acid.**—Watson Smith\* recommends the following method, worked out by J. Barnes:—2 grms. of the sample are dissolved in a 100 c.c. of warm water, in a flask capable of holding about 500 c.c.; a little sodium acetate is added to prevent any irregularity, caused by sodium chloride, which may be possibly present. A current of well-washed sulphur dioxide is now passed through the solution in excess. The liquid is then boiled until free from sulphur dioxide, allowed to cool, and diluted to 500 c.c.; 50 c.c. of this solution (= 0·2 gm. of sample) are withdrawn and mixed with 25 c.c. of a saturated solution of sodium bicarbonate, and a little starch solution. The liquid is then titrated with  $\frac{N}{10}$  iodine, each c.c. of which is equivalent to 0·00575 gm. of  $\text{As}_2\text{O}_3$ . From the percentage of  $\text{As}_2\text{O}_3$  thus obtained the amount of arsenic, as  $\text{As}_2\text{O}_3$ , found by direct titration, and calculated into  $\text{As}_2\text{O}_5$ , must be deducted. If the solution is very acid, after boiling off the sulphur dioxide, it is preferable to nearly neutralise with normal sodium carbonate before adding the bicarbonate.

Sutton, in his *Volumetric Analysis*, states that the arsenate is not completely reduced to arsenite by operating in the manner described above, and recommends W. McKay's modification of Holthof's method.† McKay mixes the arsenate solution with 20 c.c. of a saturated solution of sulphurous acid, in a bottle provided with a well-fitting, ground glass stopper, and capable of holding about 50 c.c. The stopper is firmly tied down with a piece of stout cord, and the bottle then placed in a water-bath, which is kept briskly boiling for one hour. The bottle is then removed from the bath, and, when nearly cold, opened, and the contents rinsed into a flask, diluted to 150 c.c., and

\* *Journ. Soc. Dyers and Col.*, 1884, p. 34.

† *Chem. News*, vol. liii., 1886, pp. 221, 232, 243.

concentrated to one-half. On cooling, the liquid, free from sulphur dioxide, is diluted to a known bulk, and an aliquot part titrated with iodine substantially as above. M'Kay uses  $\frac{N}{10}$  iodine.

Holthof's original method consists in heating the arsenate solution with about 100 c.c. of sulphurous acid and the same quantity of water for about four hours on a water-bath, and then boiling down over a free flame to one-half the original volume. M'Kay finds this mode of procedure to give accurate results, and apparently the only advantage of his modification is a saving in time. In many cases, however, where a number of samples have to be examined, heating gently for four hours may be preferred to boiling under pressure for one hour.

*Arsenic Acid* in sodium arsenate may also be determined by converting it into ammonium-magnesium arsenate, drying at 100° C., and weighing on a tared filter; also, by reduction as above, conversion into arsenious sulphide, and drying at 100°.

## ZINC.

**Analysis of Zinc Powder.**—*Zinc dust, zinc preparation, or zinc powder* contains, in addition to metallic zinc, variable quantities of zinc oxide, iron, cadmium, silica, &c. It is used largely as a reducing agent, principally in the dyeing of indigo. For such purposes, therefore, its value depends entirely upon the amount of metallic zinc present.

The zinc may be determined by its action upon an excess of a standard solution of potassium bichromate. For this purpose 0.661 gm. of the sample (this amount of pure zinc reduces 1 gm. of  $K_2Cr_2O_7$ ) is mixed with 80 c.c. of a solution containing 25 grms. of potassium bichromate per litre and 10 c.c. of dilute sulphuric acid. The same amount of dilute acid is added after ten to fifteen minutes, and repeated a third time; the liquid being stirred from time to time. 10 c.c. of concentrated sulphuric acid diluted with its own volume of water are now added, followed by an excess (about 10 grms.) of pure granulated ferrous ammonium sulphate. If, after well stirring, a drop of the solution does not produce a blue colour when brought in contact with a drop of potassium ferricyanide, a further weighed amount of the ferrous ammonium sulphate must be added. The excess of ferrous salt is then determined by the standard solution of bichromate. The amount of potassium bichromate reduced by 0.661 of the sample multiplied by 100 gives the percentage of metallic zinc present. Any metallic iron present will, of course, also be included.

*Example.*—0.661 gm. with 80 c.c. of a solution of potassium bichromate (25 grms. of  $K_2Cr_2O_7$  per litre) were subsequently treated with 10 grms. of ferrous ammonium sulphate. 6.1 c.c. of the same bichromate solution were required to oxidise the excess of ferrous iron. (1 gm. of ferrous ammonium sulphate = 0.1255 of  $K_2Cr_2O_7$ .)

$$0.025 \times 86.1 = 2.1525 = \text{total } K_2Cr_2O_7.$$

$$0.1255 \times 10 = 1.2550 = K_2Cr_2O_7 \text{ required by } Fe(NH_4)_2(SO_4)_2.$$

$$0.8975 = K_2Cr_2O_7 \text{ reduced by zinc.}$$

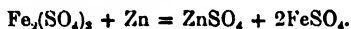
$$\therefore 0.8975 \times 100 = 89.75 \text{ per cent. of zinc in the sample.}$$

Instead of adding such a large quantity of ferrous ammonium sulphate, the operation may be modified by diluting the solution containing the excess of potassium bichromate to a given bulk, and estimating the amount of  $K_2Cr_2O_7$  still present, as given under bichromates (p. 790).

A. R. Wahl\* allows the zinc to act upon a neutral solution of ferric sulphate, and determines the ferrous salt thus produced by standard permanganate. About 0.5 gm. of zinc dust is put into a stoppered 250 c.c. flask,

\* *Journ. Soc. Chem. Ind.*, 1897, p. 15.

and mixed with 25 c.c. of cold water. When the zinc is in a state of suspension, 7 grms. of pure dry ferric sulphate are added, and the mixture gently shaken for about a quarter of an hour. 25 c.c. of strong sulphuric acid are then added, and the flask filled with water to 250 c.c. 50 c.c. of this solution are diluted with 50 c.c. of water, and titrated with  $\frac{N}{10}$  permanganate. From the amount of ferrous iron found the percentage of zinc is calculated in accordance with the following equation:—



Liebschütz\* takes 1 grm. of the sample, removes the iron by means of a magnet, and treats it with a warm, neutral solution of 5 grms. of copper sulphate. After standing for some time a little dilute sulphuric acid is added and the metallic copper well washed with water. It is then dissolved in nitric acid and the copper estimated volumetrically by titration with a standard solution of potassium cyanide. The weight of copper found multiplied by 1.032 equals the amount of zinc in the sample taken.

F. Weil† employs a standard solution of copper chloride, and after the action of the weighed sample of zinc, estimates the residual copper in solution by stannous chloride. A solution of copper chloride, containing 10 grms. of Cu per litre is prepared by dissolving 12.519 grms. of pure copper oxide (obtained by ignition of the nitrate) in a slight excess of hydrochloric acid and diluting to a litre. 50 c.c. (= 0.5 grm. of Cu) are introduced into a porcelain or platinum capsule and dilute ammonia carefully added until the liquid becomes slightly opalescent. A weighed amount (0.4 grm.) of the sample of zinc powder is now added, and a platinum wire coiled at the lower end in the form of a spiral is used to stir the mixture occasionally. When the operation is complete (known by no deposit being formed on a clean platinum wire when stirred up in the mixture) a few drops of acetic acid are added and the liquid decanted into a graduated flask holding 200 c.c. The capsule and the precipitated copper are well washed with water, and the whole diluted to the 200 c.c. mark and well mixed. After allowing any insoluble matter to subside, 20 c.c. of the clear solution are put into a small flask, mixed with 40 c.c. of pure hydrochloric acid, and titrated at the boil until completely decolourised with a solution of stannous chloride which has been standardised by the original copper solution. Subtracting the copper found in solution from 0.5 grm., the weight of copper precipitated by the zinc in the sample is obtained. This weight multiplied by 1.032, as given above, represents the amount of metallic zinc in the portion taken for analysis.

The percentage of metallic zinc may also be determined from the volume of hydrogen evolved when a weighed amount of zinc powder is treated with dilute sulphuric or hydrochloric acid.

F. Barnes, in the *Journal of the Society of Chemical Industry*, 1886, p. 145, describes a special form of apparatus for this purpose.‡

## TANNIC ACID AND TANNINS.

**Analysis of Tannins.**—A great variety of processes have been devised for estimating tannic acid in the substances known as "*Tannins*." The majority of the published methods have had the valuation of tannins for tanning leather mainly in view, but it does not necessarily follow that these methods are equally serviceable for valuing tannins used in dyeing.

\* *Journ. Amer. Chem. Soc.*, vol. vii., p. 136.

† *Chem. News*, vol. liv., 1886, p. 314.

‡ See also F. Meyer, *Journ. Soc. Chem. Ind.*, 1894, p. 341.

Procter's modification of Löwenthal's process\* has been very generally adopted both for tanning and for dyeing purposes. For estimating tannins used in the leather industries, however, the process has been almost entirely superseded by the gravimetric hide-powder processes.†

*Löwenthal's Gelatin-permanganate Process.*—The tannic acid is estimated by oxidation with a standard solution of potassium permanganate, using a known volume of a solution of indigo-sulphonic acid as an indicator. The operation is performed in two stages. In the first place the total oxidisable matters are determined, and in another portion of the solution the tannic acid is precipitated by gelatin, and the oxidisable matters other than tannin are estimated in the filtered solution. The difference between the two titrations expresses the amount of tannic acid in terms of standard permanganate. In precipitating the tannic acid by gelatin, Procter saturates the solution with salt. Hunt‡ has shown that a considerable amount of gallic acid is likewise precipitated under these conditions, and recommends that the liquid be only one-quarter saturated with salt. Unfortunately some of the tannic acid is thereby left in solution. Rawson has made a considerable number of experiments from a dyer's point of view, comparing the results obtained by various modifications with practical results in dyeing. His mode of working the process will be here given, although it differs but little from either Procter's or Hunt's methods.§

The following solutions are required:—

*Standard Permanganate.*—A  $\frac{N}{50}$  solution of potassium permanganate is prepared by dissolving 0.632 grm. of the pure recrystallised salt in a litre of water. The solution is standardised by pure ferrous ammonium sulphate (p. 792), or pure oxalic acid (p. 766). Each c.c. = 0.00126 grm. of crystallised oxalic acid.

*Indigo Solution.*—1 grm. of pure indigotin is dissolved in 50 c.c. of pure concentrated sulphuric acid, and diluted with water to 1000 c.c.

*Gelatin Solution.*—20 grms. of fine gelatin (Nelson's) are soaked in water for two or three hours, and then dissolved on the water-bath in a litre of water. The liquid is saturated with salt and filtered.

*Sulphuric Acid and Salt.*—A 5 per cent. solution of sulphuric acid is saturated with sodium chloride.

*Titration for Total Oxidisable Matters.*—About 2 grms. of the sample (more or less according to the amount of tannin probably present) are boiled with 500 c.c. of distilled water in a flask for half an hour. The liquid is quickly cooled, 5 c.c. of a 10 per cent. solution of acetic acid added, and diluted to 500 c.c. After shaking well, it is poured into a glass cylinder and the insoluble matter allowed to subside. [The decoction should not be filtered, since filter paper absorbs tannic acid to a considerable extent, and the amount abstracted from solution depends upon the rate of filtration.] When the insoluble matters have sufficiently subsided, which may take an hour or so, 10 c.c. of the clear solution are carefully withdrawn and mixed with 500 c.c. of water in a large porcelain basin, 25 c.c. of the indigo solution are added, and  $\frac{N}{50}$  permanganate run in from a burette in continuous drops during constant and vigorous stirring until the liquid becomes of a light green colour. The permanganate is now added more slowly until the green colouration has given place to yellow, when usually a faint, but unmistakable, pink rim may be

\* *Journ. Soc. Chem. Ind.*, 1884, p. 82; and 1886, p. 79

† *Journ. Soc. Chem. Ind.*, 1887, p. 94; 1906, pp. 1193 and 1203; 1907, pp. 79, 455, and 1186. *Journ. Soc. Dyers and Col.*, 1907, p. 237.

‡ *Journ. Soc. Chem. Ind.*, 1885, p. 263.

§ For details of these methods, see the papers above mentioned; and for fuller particulars, also Procter's *Text-Book of Tanning*, Allen's *Commercial Organic Analysis*, vol. iii., and Sutton's *Volumetric Analysis*.

observed. 25 c.c. of the indigo solution with 500 c.c. of water are titrated alone, and the number of c.c. of permanganate deducted from the result. The difference expresses the total amount of oxidisable matters in 10 c.c. of the decoction.

**Titration of Oxidisable Matters other than Tannin.**—50 c.c. of the clear decoction are introduced into an 8-oz. stoppered bottle and mixed with 25 c.c. of the gelatin and salt solution and 25 c.c. of the acid salt solution, and well shaken. The liquid is thus practically half saturated with salt. After half an hour or so it is filtered and 40 c.c. of the filtrate (= 20 c.c. of the original solution) mixed with 500 c.c. of water and 25 c.c. of the indigo solution, and titrated with permanganate, as before. If there is a difficulty in obtaining a perfectly clear filtrate, a little kaolin or barium sulphate may be shaken up with the liquid before filtering. In the case of myrabolans and sumach, however, the filtrate is usually perfectly clear without any addition of this kind.

*Example.*—2 grms. of myrabolans were extracted and made up to 500 c.c., as above described. 10 c.c. titrated direct with 25 c.c. of the indigo solution required 29.5 c.c. of  $\frac{1}{10}$   $\text{KMnO}_4$ . 25 c.c. of indigo alone required 16.5 c.c. of  $\frac{1}{10}$   $\text{KMnO}_4$ .

Total oxidisable matters in 10 c.c., therefore, equal to  $29.2 - 16.5 = 13$  c.c. of  $\frac{1}{10}$   $\text{KMnO}_4$ .

40 c.c. of the filtrate from gelatin precipitate (= 20 c.c. of the original solution) required with 25 c.c. of indigo solution 23.2 c.c. of  $\frac{1}{10}$   $\text{KMnO}_4$ .

Oxidisable matters other than tannin in 20 c.c., therefore, equal to

$$\begin{aligned} 23.2 - 17^* &= 6.2 \text{ c.c. of } \frac{1}{10} \text{ KMnO}_4 \\ &= 3.1 \text{ ,, ,, in 10 c.c.} \end{aligned}$$

Therefore,  $13 - 3.1 = 9.9$  c.c. of  $\frac{1}{10}$   $\text{KMnO}_4$  consumed by the tannic acid in 10 c.c. of the infusion. The percentage of tannin is commonly expressed in terms of oxalic acid.

$$\frac{0.00126 \times 9.9 \times 50 \times 100}{2} = 31.18 \text{ per cent. of tannic acid expressed as oxalic acid.}$$

According to Neubauer & Oser, 0.063 of oxalic acid corresponds to 0.04159 of gallo-tannic acid (gall-nut tannin) or 0.06235 of querci-tannic acid (oak-bark tannin). The percentage of tannic acid expressed in terms of oxalic acid multiplied by 0.666 gives, therefore, the percentage of gall-nut tannin; and multiplied by 0.99 the percentage of oak-bark tannin.

**Commercial tannic acid** and extracts of sumach, myrabolans, &c., are examined in the same manner as natural tannins, the boiling with water being omitted. About 1 grm. of tannic acid or 2 to 5 grms. of "extracts" dissolved in 500 c.c. of water will give solutions of convenient strengths.

In place of gelatin, specially prepared *hide-powder* is often used to precipitate the tannin matters. 50 c.c. of the decoction of tannin are treated with 3 grms. of hide-powder for a period of 18 hours (shaking occasionally) and then filtered. 10 or 20 c.c. of the clear filtrate are then titrated, as above described. Concordant results are obtained, but on account of oxidisable substances other than tannin being abstracted from solution, the method cannot be recommended for dyeing purposes.

In the *Journal of Society of Chemical Industry* (1887, p. 94), Procter†

\* 0.5 c.c. of  $\text{KMnO}_4$  is here allowed for the action of oxidisable matters introduced by the gelatin. This should be determined by means of a blank experiment.

† Since that date Procter has contributed several papers on the subject of Tannin Analysis to the Society of Chemical Industry. One of the most recent appears in the *Journal of the Society*, 1907, p. 79, and is entitled "The Present Development of the Analysis of Tannin Materials," by H. R. Procter and H. G. Bennett. The methods here given were embodied in the official process of Tannin Analysis of the International Association of Leather Trade Chemists, a description of which will be found in the *Journal of the Society of Dyers and Colourists*, 1907, p. 237.

describes a gravimetric process for estimating tannic acid. 50 c.c. of a clear decoction of the tannin (containing about 1 per cent. of tannin) are evaporated to dryness at 100° C. and weighed. About 100 c.c. of the same solution are filtered by upward filtration through a layer of 5 grms. of hide-powder contained in a glass tube. 50 c.c. of this filtrate deprived of its tannin are evaporated under the same conditions and weighed. The difference between the two results represents the amount of tannin in 50 c.c. Gallic acid and other bodies of no value in dyeing, however, are likewise partially withdrawn from solution, and, therefore, for dyeing purposes the same objections are attached to the process as in the volumetric method where hide-powder is used.

As an example the following case may be quoted. A sample of solid myrabolan extract which had undergone a considerable change during concentration gave by the gravimetric hide-powder process 51 per cent. of tannin. By the gelatin-permanganate process only 18.5 per cent. of gallo-tannic acid was obtained. The correctness of the latter figure was confirmed by dye-trials, in which the original myrabolans were used for comparison. For dyeing purposes the solid extract was found to be of far less value than the original nuts, which only gave 30 per cent. tannin by the hide-powder process against 51 per cent. in the extract.

Gerland determines tannin by means of a solution of tartar emetic prepared by dissolving 2.611 grms. of the crystals dried at 100° C. in 1 litre of water. A few grains of thymol will preserve the liquid for a considerable time. 1 c.c. = 0.005 gm. tannin. 50 c.c. of the tannin solution are taken for titration, 2 grms. of ammonium chloride added, and titrated with the solution of tartar emetic until no further turbidity is produced. The titration is finished when a drop of the antimony solution ceases to cause a turbidity with a drop of the tannin solution placed on a piece of black glass.

Becker\* has devised the following process:—5 grms. of Methyl violet are dissolved in 1 litre of hot water, and, when cold, filtered. 10 grms. of the purest tannin, well dried, are dissolved in water and made up to 1 litre. 10 grms. of the sample of tannic acid (or 20 to 40 grms. of sumach, &c.) are also dissolved and made up to 1 litre, the moisture having been previously determined.

50 c.c. of the Methyl violet solution are run from a burette into a beaker, and, with 450 c.c. of water, heated to 50° C. The pure tannin solution is then slowly dropped in from a second burette, stirring well until all the colouring matter is thrown down. This is ascertained to be the case when a small portion gives a colourless filtrate. If the filtrate is still coloured it is poured back to the bulk and more tannin solution added. Good filter paper must be used, otherwise the liquid passes through turbid. When it has thus been found how much pure tannin is needed to decolourise 50 c.c. of the coloured liquid, the solution of tannin under examination is treated in the same way, and its relative value is calculated from the figures obtained.

P. Wilhelm† makes use of a solution of Methylene blue and recommends the following mode of procedure:—A solution of Methylene blue is prepared by dissolving 12.5 grms. of the colouring matter, free from zinc, in a litre of water. This is standardised by a solution of pure tannic acid, 19.6 grms. per litre. 20 c.c. of the Methylene blue solution are mixed with 10 c.c. of dilute ammonia (1.25 ammonia per litre) and tannic acid run in until all the Methylene blue has been precipitated, which point is ascertained by spotting a piece of filter paper with a drop of the solution. It was found that 10 grms. of *pure* Methylene blue were precipitated by 4.9 grms. of pure tannic acid, which is in accordance with theory. Having determined the amount of pure tannic acid

\* *Chemical News*, vol. li., p. 229.

† *Journ. Soc. Chem. Ind.*, 1898, p. 957.

necessary to precipitate a certain amount of Methylene blue, the value of any tannin sample is readily found. The tannin solution to be tested should be approximately of the same strength as the tannic acid solution above mentioned.

Procter considers "that with such varied and little understood bodies as the tannins, the mode of analysis must be chosen in the relation to the use to which the materials are to be put. If the object is to precipitate antimony, naturally Gerland's tartar emetic process is more likely to give good results than a gelatin process. If ink making or dyeing black is the requirement, Handke's process with ferric acetate, or a colorimetric method, would suggest itself. If fixing aniline colours is required, an aniline colour, such as Methyl green, may be used as a precipitant. In all these methods we are not really determining the quantity of a given ingredient present, but the activity in a special direction of a mixture of various compounds. It is, therefore, most essential that the chemist should specify not only his results but also how his results are obtained. In the case of most tannin materials the sampling, grinding, and extraction are as important and as likely, if unsystematically carried out, to lead to discrepancies as any other part of the process."

**Examination of Tannins by Dye-trials.**—Whatever method of analysis is used for estimating tannic acid, the results should always be confirmed by making experimental dye-tests. The exact mode of procedure may vary according to the kind of tannin under examination and the uses to which it is to be put, but the following can be recommended for general purposes:—2 grms. of each sample (myrabolans, sumach, &c.) are boiled for fifteen minutes with half a litre of water. The decoctions (with insoluble portion) are made up exactly to 500 c.c., and poured into beakers, which are then introduced into a steam bath as described on p. 810. 10 grms. of common salt are added to each beaker, and when the temperature is uniform (about 95°), 10 grms. of cotton yarn (previously thoroughly wetted) are introduced. The yarn is worked on glass rods dipping beneath the surface of the liquid, and the solutions allowed gradually to cool. After three hours (or more) the yarn is taken out and the excess of liquid removed (not washed), and each hank introduced into separate beakers, containing 200 c.c. of basic ferric sulphate (nitrate of iron), of specific gravity 1.01 (2° Tw.). After fifteen to twenty minutes the yarn is taken out, washed, dried, and the depth of shade compared. It is most important that in each series of tests, the conditions as to temperature, time, amount of water used, &c., should be exactly the same for each sample.

## TURKEY-RED OIL.

**Examination and Analysis of Turkey-Red Oil.**—A good sample should not show any appearance of oily drops on diluting with ten times the volume of tepid water, even after standing some hours. No turbidity ought to appear on diluting the oil with a considerable amount of aqueous ammonia. A turbidity indicates the presence of solid fats, and proves that in the manufacture of the article either very impure castor oil or other crude oils (rape, sesame, cottonseed, olive, and train oils), or mixtures of these have been used, all of which contain palmitin and stearin.

An alcoholic solution of Turkey-red oil is the more turbid the more unaltered oil it contains.

**Estimation of Total Fatty Matter.**—This determination is of considerable importance, and is carried out by Breinl\* as follows:—A flask of 200 c.c. capacity, having a long neck and graduated to  $\frac{1}{10}$  c.c., is required. 30 grms. of

\* *Journ. Soc. Chem. Ind.*, 1889, p. 573.

the sample are accurately weighed off and washed into the flask with hot water, the volume made up to about 100 c.c., then 25 c.c. of sulphuric acid of specific gravity 1.56 are added, and the mixture heated to boiling, with frequent shaking until the fatty matter forms a clear and transparent layer. A hot concentrated solution of common salt is next added in small portions until the separated layer of fat rises above the lowermost mark. After cooling, the volume is read off, the number of c.c. multiplied by 3 corresponds to the percentage of total fatty matter.

J. A. Wilson\* has devised the following method for estimating the total fatty matter:—10 c.c. of saturated salt solution are run into a globular separator, and 5 to 6 grms. of the sample poured into the separator. About 5 c.c. HCl (1:1) are then added, and the whole thoroughly agitated with 25 c.c. ether; the acid solution is run off and again treated in another separator with 25 c.c. more ether, and after separating from the aqueous layer it is added to the first ether extract. The ether is then evaporated and the fatty matter in the flask dried by blowing air through for about ten minutes. 30 c.c. of absolute alcohol are then added, the solution agitated and allowed to stand for a short time, poured through a dry filter, the residue in the flask washed three times with alcohol, and all received through the filter into a tared flask; the alcohol is evaporated and the fatty acids dried on the water-bath about an hour, whilst a current of air is passed through the flask. The residue is then weighed and the percentage calculated.

*Neutral Fat.*—Benedikt and Lewkowitsch† proceed as follows:—About 30 grms. of the sample are dissolved in 50 c.c. of water, 20 c.c. of ammonia and 30 c.c. of glycerin are added, and the mixture exhausted with ether twice, using 100 c.c. each time. The ethereal solution is freed from small quantities of dissolved soap by washing with water, and transferred to a tared wide-mouthed flask. After evaporating the ether, the residue is dried at first on the water-bath, then in an air-bath at 100° C., and weighed.

*Soluble Fatty Acids (Sulphonated Fatty Acids).*—About 10 grms. of the oil are dissolved in a stoppered bottle in 25 c.c. of water, 25 c.c. of fuming hydrochloric acid are added, and the bottle is heated in an oil-bath to 140° C. for one hour. Water is added after cooling, the mixture transferred to a beaker, and the fatty layer filtered off through a moistened filter, and the fat washed with hot water into a 250 c.c. flask. After cooling, the liquid is run through a dry filter to eliminate any particles of fat, and 200 c.c. of the filtrate treated with barium chloride. From the amount thus found, after multiplying by five-fourths, the quantity of sulphuric acid (see below), as determined in the following test, is subtracted, and the difference calculated to ricinoleic acid, 80 parts of SO<sub>3</sub>, corresponding to 378 parts of ricinoleo-sulphuric acid, C<sub>18</sub>H<sub>35</sub>O<sub>2</sub>. O. SO<sub>3</sub>H. The molecular weight of hydroxystearo-sulphuric acid being 380, the calculation will remain the same, even if other oils were used in the preparation of the Turkey-red oil.

*Sulphuric Acid.*—The quantity of sulphuric acid present in the form of ammonium or sodium sulphate is found by dissolving a weighed quantity of the sample in ether, and shaking it several times with a few c.c. of saturated salt solution (free from sulphate). The whole of the washings are united, diluted, filtered, and the filtrate precipitated with barium chloride.

*Ammonia and Caustic Soda.*—10 grms. of the sample are dissolved in a little ether, and extracted four times with dilute sulphuric acid (1:6), using 5 c.c. each time.

For the determination of ammonia the acid liquors are distilled with caustic potash, and the vapours absorbed in a measured quantity of standard

\* *Journ. Soc. Chem. Ind.*, 1891, p. 26.

† *Oils, Fats, and Waxes.*



acid; after titrating back the excess of acid, the amount of ammonia is calculated.

For the estimation of *caustic soda* the acid liquors are concentrated in a platinum dish on the water-bath, and the excess of sulphuric acid driven off by heating on the sand-bath; the residue is mixed with ammonium sulphate, ignited, and the residue of sodium sulphate weighed.

*Iron* is determined, according to Emde,\* by shaking up a quantity of the oil in a graduated cylinder with dilute sulphuric acid. A few drops of potassium ferrocyanide are added, and the whole shaken up with a little ether. The oil dissolves in the ether, and forms a sharply defined layer on the water. If iron be present, a more or less dense layer of Prussian blue, containing all the iron, will appear at the line of contact of the two liquids. If in comparative tests the same quantities of oil, water, acid, and potassium ferrocyanide be used, the density of the colouration will show roughly the amount of iron present. For accurate determinations the iron is precipitated with ammonia as hydrate, and weighed as ferric oxide.

*The ash* may be estimated by burning a quantity of the oil at a low temperature in a platinum basin, and weighing the residue. The amount ranges from 0.1 to 0.3 per cent.

Bensemann recommends taking the *melting point of the fatty acids*, after treating the oil with dilute hydrochloric acid, shaking out with ether, washing out the excess of hydrochloric acid, evaporating off the ether, and drying the residue, which consists of fatty acids and unaltered oil. This gives a good idea as to the nature of the oils used for manufacturing the Turkey-red oil, even if mixtures are present. Thus the melting point of the mixture of fatty acids from cotton-seed oil lies between 42° to 43° C., from olive oil 26° to 27° C., from rape oil 21° to 22° C.; whilst the castor oil acid remains liquid below 0° C.

## ANILINE OIL AND ANILINE SALTS.

**Analysis of Aniline Oil.**—Pure commercial aniline oil contains traces of insoluble hydrocarbons, orthotoluidine, and sometimes traces of sulphuretted hydrogen, nitrobenzene, benzene, ammonia, and amidothiophene. A good sample should not contain above 1 per cent., and most of them rarely contain more than 0.5 per cent., of water. The specific gravity is ascertained by means of the specific gravity bottle.

To find the boiling point of a sample, R. J. Friswell† proceeds as follows:—250 c.c. of the aniline oil are distilled in a flask with side tube through a condenser into a 250 c.c. graduated cylinder. A few pieces of platinum wire previously dropped into the flask cause the liquid to boil more regularly. The flask should be held by a clamp above the side tube *directly* over a small flame. A good thermometer should be suspended by means of a cork in the neck of the flask, the top of the bulb being placed just below the side tube. It is usual to take the temperature at which the first drop of distillate falls off the end of the side tube.

The temperature of the ascending vapour is carefully observed and recorded at the completion of every 25 c.c. (*i.e.*, 10 per cent. of the whole), any fluctuation being specially noted. The temperature of the thermometer when the flask becomes *just dry* is also of importance.

*Insoluble oils* may be detected by dissolving 10 c.c. in an equal volume of hydrochloric acid and diluting with water to 100 c.c. The best samples show

\* *Journ. Soc. Chem. Ind.*, 1888, p. 591.

† *Thorpe's Dictionary of Applied Chemistry*, vol. i., p. 166.

only a slight opalescence when thus treated, and the smell of the insoluble oils, nitrobenzene, naphthalene, &c., is always distinguishable. Friswell also states that on violently shaking the sample of aniline for a few minutes the smallest trace of nitrobenzol may be distinguished by the froth assuming a distinct yellow colour.

*Water.*—Liebmann and Studer\* estimate the water as follows, the boiling point being determined at the same time. 100 c.c. of the aniline are distilled and the first 10 c.c. of the distillate collected separately. To this is added 1 c.c. of saturated salt solution, the mixture well shaken, allowed to settle, and the volume of salt solution read off. Aniline oil, containing 0.3 per cent. water, causes no increase in volume of the salt solution, consequently 0.3 c.c. must always be added to the amount of salt solution observed. The specific gravity at 15° C. is taken on the remaining part of the distillate after removal of the water. This varies in good oils from 1.0265 to 1.027. At least 80 per cent. of the oil should boil within  $\frac{1}{2}$ ° C. of 183° C.

*Sulphur compounds*, if present, are evolved as sulphuretted hydrogen when the sample is boiled. If, during the distillation, a paper moistened with lead acetate exposed to the vapour (not immersed in the oil) be coloured light brown, traces of sulphur are present. Should the paper be blackened, the quantity of sulphur is determined by boiling a weighed amount of the oil, using a reversed condenser and passing a current of carbon dioxide through the apparatus, the gas being bubbled through a known volume of  $\frac{N}{10}$  silver nitrate. The silver sulphide is filtered off and the filtrate titrated with hydrochloric acid. The difference is calculated to silver sulphide and eventually sulphur.

*Determination of Aniline in presence of small quantities of Toluidine and vice versâ.*—Reinhardt's method† for the estimation of aniline, *o*- and *p*-toluidine in commercial aniline oil, is founded on the following reactions:—

When a solution of aniline in dilute acid is treated with a mixture of potassium bromide and bromate it is converted into tribromaniline, whilst *o*- and *p*-toluidine under similar treatment yield dibromo derivatives. The brominating solution is prepared from 480 grms. of bromine, 336 grms. potassium hydrate (100 per cent.), and 1 litre of water; the solution is boiled for two to three hours and then diluted to 9 litres.

In conducting an analysis 1.5 to 2 grms. of the oil are dissolved in a mixture of potassium bromide and hydrochloric acid equivalent to 100 c.c. of hydrobromic acid (specific gravity 1.46) and 1,000 c.c. of distilled water, and the brominating solution is added until a reaction is obtained with potassium iodide and starch paper.

The brominating solution being standardised against pure aniline, the toluidine value is obtained by multiplying the aniline value by  $\frac{160.5}{93}$ .

When an oil contains only aniline and the two toluidines, and is free from water, one titration gives the amount of the constituents according to the following equation:—

$$x = 2.3777 vt - 1.3777 a,$$

in which *a* = weight of oil taken, *x* = amount of aniline, *t* = value of the brominating solution calculated on pure aniline, and *v* = the number of c.c. of brominating solution taken. Then *a* - *x* = amount of toluidine contained in the oil.

In the case of toluidine containing small quantities of aniline the bromine solution is titrated against pure toluidine and the aniline value *t* is calculated

\* *Journ. Soc. Dyers and Col.*, 1899, p. 107.

† *Journ. Soc. Chem. Ind.*, 1893, p. 954; see also Dobriner and Schranz, *Journ. Soc. Chem. Ind.*, 1896, p. 298.

by multiplying it by  $\frac{93}{160.5}$ . It is, indeed, preferable to designate the value of the brominating solution in c.c. against pure aniline as  $t$ , and against pure toluidine as  $T$ , then the amount of aniline is given by the equation—

$$\frac{x}{t} + \frac{x-a}{T} = v.$$

The method can also be employed for the valuation of aniline hydrochloride, which for the purpose of analysis must be dried over sulphuric acid. The formula becomes

$$X = 2.5102 VT - 1.5102 A, - A.$$

$X$  and  $V$  have here also corresponding values to those given above.  $T$  is the value of the brominating solution in pure aniline hydrochloride, and is obtained from the aniline value  $t$  by multiplying by  $\frac{129.5}{93}$ .

The end of the reaction is detected by spotting on starch-iodide paper. With *p*-toluidine it is advisable to run in the brominating solution slowly at the beginning and towards the end of the reaction. About 150 c.c. of the brominating solution (1 litre = 8 grms. of aniline) are taken for a determination, the readings being observed very carefully at 15° C.

**Analysis of Aniline Salt (Aniline hydrochloride).**—The following points require consideration\* :—

1. Quality of oil used in the preparation of the salts.
2. Amount of water present.
3. Amount of free acid present.
4. Adulterations.

If the crystals are of a large, flat, well-developed shape, it may be taken for granted that the salt has been prepared from pure aniline oil. If otherwise, or in the form of powder, the salt is decomposed by means of caustic soda and the liberated aniline submitted to the distillation test described above.

**Water** is estimated by allowing a weighed quantity of the salt to remain for twenty-four hours in a desiccator and weighing again.

**Free Acid.**—5 grms. of the sample are dissolved in 10 c.c. of distilled water. To this solution 5 drops of a solution of Crystal violet (1 gm. per litre) are added, and the change of colour is compared with that of a solution of 5 grms. of pure aniline salt treated in the same way. If the solution of the sample is bluer than the pure salt solution it is titrated with a decinormal aqueous solution of aniline until the colour of the two solutions is the same. The amount of aniline solution thus required represents the free acid present in the sample.

## EXAMINATION AND ANALYSIS OF DYES.

**Comparative Dye-tests.**—Generally speaking, the most satisfactory method of valuing dyes is by means of carefully conducted experimental dye-trials. It is most important that the tests be made under identical conditions, since, in many cases, a slight variation in temperature or volume of water used causes a considerable difference in the results. A convenient form of apparatus consists simply of a rectangular copper vessel, measuring about 18 ins. long, 12 ins. wide, and 8 ins. deep. Six circular holes, about  $4\frac{1}{4}$  ins. diameter, are cut out of the top to receive the dye-vessels. These are preferably glass beakers of  $\frac{1}{4}$ ,  $\frac{1}{2}$  or 1 litre capacity, which fit into the copper vessel resting on india-rubber

\* Liebmann and Studer, *Journ. Soc. Dyers and Col.*, 1899, p. 108.

rings. The vessels (beakers) should be as nearly as possibly of the same size. They are heated by means of steam, evolved from water kept briskly boiling in the copper bath. A slightly higher temperature in the dye-vessels may be attained by adding common salt, or some other salt—*e.g.*, calcium chloride—to the water in the copper bath; but for all ordinary purposes where glass beakers are used no addition is required. Fletcher's tube-burner, No. B 24, is recommended for boiling the water in the copper bath.

Sometimes earthenware pots are used in place of glass beakers, but on account of the thickness of the vessels it becomes necessary to use either strong saline solutions, oil or glycerin in the copper bath. The water in the dye-pots, however, does not usually get heated regularly, and in order to overcome this difficulty, as well as to reduce the risk of fire attendant on the use of an ordinary oil bath, R. L. Whiteley\* has devised an improved bath, which is shown in Fig. 119.

It is made in two parts. The lower portion (*a*), made of copper welded and brazed together, measures  $21\frac{1}{2}$  in.  $\times$   $15\frac{1}{2}$  in.  $\times$  6 in. and has an internally-

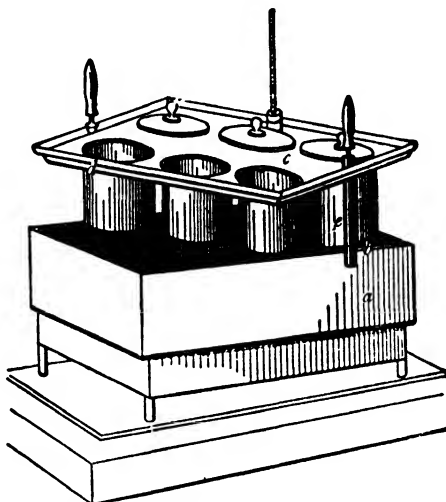



Fig. 119.—Whiteley's oil bath for dye-testing.

projecting rim, *b*, so that in case the temperature should rise to the boiling point of the oil, it will be thrown towards the centre. The upper portion of the bath, *c*, fits into the lower by means of the rim, *d*, which projects downwards about  $\frac{3}{4}$  in. In this portion, which is tray-shaped, six copper cups (5 ins. deep and  $5\frac{1}{2}$  ins. wide) are fixed to receive the dye-pots. The space between the dye-pot and the cup is filled with glycerin. The tray is provided with an aperture for a thermometer, and at each end projects a handle by means of which the flaps, *e*, can be moved and the oil stirred so as to equalise the temperature. Cotton-seed oil is recommended to be used for the copper bath, which is heated to a temperature of  $160^{\circ}$  to  $170^{\circ}$  C. by means of a set of three Wright's No. 310 burners.

In making experimental dye-tests the amount of dye used in comparison with the material to be dyed must be small—not nearly sufficient to produce what may be termed a full shade. In the first place, it is difficult to discriminate between deep shades of colour; and, again, if too much dye be used, much of it may be left in the baths, and probably in unequal quantities. The

\* *Journ. Soc. Chem. Ind.*, 1891, p. 521.

material to be dyed is best suspended in the vessel by means of a glass-rod bent thus—. The yarn or cloth, quite free from oil and other impurities, is previously thoroughly wetted out, so as to guard against unevenness, and frequently and regularly turned, by means of a straight glass-rod, during the course of one to two hours, as circumstances require. The exact mode of procedure varies, of course, according to the properties of the colouring matters to be examined, and the purposes to which they are to be applied. As a rule, the method employed should be similar to that which is followed on the large scale, although, in certain cases, slight modifications may be introduced with advantage. In testing dyewoods, alizarin colours, and other colours for which mordants are required, for example, it is preferable to use rather a larger proportion of the mordant than would be found necessary to dye a good shade on the large scale. The material to be used in making the dye-trials depends, to a certain extent, upon the application of the colouring matters under examination. The woollen-dyer may use either slubbing, yarn, or cloth, but, for most purposes, fine botany yarn will be found most convenient. Even the cotton-dyer may frequently find it advantageous to make his dye-tests upon worsted yarn, since many colouring matters which may be applied to the dyeing of either wool or cotton are taken up by the wool fibre much more completely, and, consequently, less colour is left in the bath. It is most important that the dye-bath should be exhausted as completely as possible, otherwise more colour may be left in solution in one case than in another. Many of the dyestuffs are taken up by wool and silk so completely that the dye-bath is quite colourless. Other colouring matters, however, cannot be completely withdrawn from their solutions in this manner, and, in such cases, it is necessary to dye a second, and perhaps even a third lot of material without a further addition of colour. Among the dyes which are not easily withdrawn from solution may be mentioned Picric acid, Malachite green, Alkali blue, archil and cudbear, sulphide colours, indigo, and other vat colours.

For the dye-vessels which have been already mentioned ( $\frac{1}{2}$  litre capacity), 10 grms. of worsted yarn or cloth, or 20 grms. of cotton yarn, will be found a convenient quantity, but in the case of cotton dyeing it is preferable for the sake of uniformity to employ vessels of 250 c.c. capacity and to dye 10 grms. In the case of coal-tar colours about 0.5 per cent. (varying according to circumstances) of the dye, calculated on the weight of the material, should be used. The requisite amount of colouring matter should not be weighed out direct and added to the dye-baths, but standard solutions should be made by dissolving 1 grm. of each sample in a litre of water. Each c.c. of such a solution would contain 1 milligramme of colour, and, consequently, 100 c.c. on 10 grms. of material would correspond to 1 per cent.

If it be required to ascertain which is the cheapest of two or more samples of dyes of a similar kind, the simplest plan is to dye equal weights of material with quantities in inverse proportion to their prices. For example, supposing that three samples of azo-scarlets at 10d., 1/-, and 1/4 per lb., respectively, are to be examined. Three lots of yarn, each weighing 10 grms., are dyed respectively with 0.8 per cent. of the first sample at 10d. per lb., 0.66 per cent. of the second at 1/- per lb., and 0.5 per cent. of the third at 1/4 per lb. These quantities represent equal money values, and, therefore, that swatch or hank which comes out the best in the dye-trials will be the cheapest. It might be mentioned here that in dyeing such colours as azo-scarlets,  $2\frac{1}{2}$  per cent. of sulphuric acid and 10 per cent. of sulphate of soda should be added to each bath. If the relative value of two or more samples of colouring matter be required, the problem is not quite so simple. In the first place, equal quantities of material—wool, cotton, or silk, as the case may be—are dyed respectively with equal weights of the various samples. After washing and drying, the swatches

or hanks are compared, and a second series of tests made, using a greater quantity of those samples which produced lighter shades, or less of those which gave deep shades, according to what is judged will be sufficient to yield the same depth of shade in all cases. It will generally be found necessary to make three, or perhaps four, series of tests in this way. It is sometimes recommended to attain this end in one series of tests, by adding more colouring matter from time to time, as occasion requires, to those baths which produce lighter "shades" and by continuing the dyeing until all the patterns have acquired the proper degree of saturation and appear of the same shade. This plan, although occupying considerably less time, does not give such reliable and satisfactory results as the process which has been already described. The relative value of the samples will be in the inverse proportion of the amount of dye required to produce the same shade. For example, if with two samples of Magenta, 56 c.c. of one produced the same depth of shade as 70 c.c. of the other, their relative value would be as 70 : 56, or expressed centesimally as 100 : 80. It must be borne in mind that such valuations are only strictly accurate when the various samples under examination are of the same tone; a pure bright colour being more valuable, of course, than a dull one. In the case of Rosaniline blue, for instance, the red shades are not so valuable as the pure or greenish shades of blue. Artificial light is of great service in comparing many shades, especially for green, blue, and violet, since by these means certain peculiarities are brought out very distinctly. Thus a blue with a slight cast of red appears almost violet in gas or candle light, while a blue with a slight shade of green appears distinctly bluish-green. Whenever a fresh lot of dye requires comparing with an old standard, it is always necessary to make a dye-trial of that standard *at the same time*, for, however careful one may be to work under the same conditions, dye-tests made at different times with the same sample may vary slightly in character. From what has been previously stated, it is scarcely necessary to mention that in testing those colouring matters which require mordants, the cloth or yarn must be prepared in a similar manner to that which is dyed on the large scale. It is of the greatest importance that the cloth or yarn should have been mordanted at the same time and under identical conditions—preferably in one bath. In all cases the material used—cotton, wool, or silk—should be of exactly the same quality for each series of tests.

**Colorimetry.**—In certain cases, the relative value of dyes may be ascertained by making colorimetric observation of their solutions, but the results cannot be considered as reliable and satisfactory as comparative dye-trials. The impurities present in many dye-wares render the observations somewhat difficult and obscure. Whilst many of the coal-tar colours may be estimated fairly accurately by "colour titration," others—especially yellows, oranges, and scarlets—do not always give results which are confirmed by dyeing. In other words, two colours may give a similar shade and depth of tint in solution, and produce very different effects in dyeing and *vice versa*. A good colorimeter, however, will be found very useful in the examination of dyes as a preliminary step, or in some cases as a check upon the dye-tests.

There are various forms of apparatus designed for this purpose, and the methods of working differ to some extent, but the principle is the same in all cases. Among other useful colorimeters may be mentioned those of Mills, Laurent and Ridsdale. A simple and useful instrument consists of two graduated Nessler tubes, each being provided with a stopcock near the base. The solutions to be examined must be very dilute, otherwise it will be found impossible to discriminate between a small difference of intensity of two solutions. In the case of pure coal-tar colours, the solutions to be used for 100 c.c. cylinders, should contain only 2 to 5 milligrammes of colouring matter per litre. In examining two solutions, 100 c.c. of each are placed in the Nessler glasses,

and, on looking through the liquids downwards, if one appears darker than the other, a little is carefully run off until the two solutions appear of the same intensity. The volume of the liquid in each tube is observed, and the figures will denote the inverse ratio of the value of the two samples. Suppose for example, that equal weights of two samples of Magenta were dissolved in equal volumes of water, and that 75 c.c. of the one gave the same depth of colour as 100 c.c. of the other, the relative value of the two samples would be as 100 : 75. It will, of course, be understood that the two cylinders or Nessler glasses must be of the same diameter throughout their entire length. The ordinary plain Nessler tube may be used for the same purpose in the following manner:— Solutions of the dyes are made of about ten times the strength of those above mentioned. In the case of Magenta, &c., 50 milligrammes per litre will be found a convenient strength. Having prepared the solution, 10 c.c. of the standard are run into a Nessler glass and diluted with distilled water to the mark (100 c.c.), and more or less of the other solution is measured into a second glass, diluted in a similar manner, until the same depth of colour is reached in both tubes. The relative value of the two samples will be in inverse proportion to the number of c.c. required.

In connection with this subject, the Tintometer, an instrument for the analysis, synthesis, matching, and measurement of colour, devised by J. W. Lovibond,\* might be mentioned here. The instrument not only serves the purpose of a colorimeter, but also of a colour recorder. The apparatus, apart from stands and reflectors, may be divided into two essential parts; the first is an instrument giving two fields of view under exactly similar monocular conditions, freed from the errors arising from unequal side lights, and the different power of distinguishing which may exist in the eyes of the observer. The second part consists of standard sets of coloured glass slips, the glasses composing each set being all of the same colour, but regularly graded for depth of tint; each series of one colour bearing a denominational or "colour number"; the depth of tint being also noted on the slips by an additional "tint number" engraved on the slip below the colour number. The use of several superimposed glasses from a single set produces a depth of tint represented by the aggregate of tint numbers on the glasses used, while glasses from several sets produce a composite colour, and the exact proportion of each colour can be read off.

The instrument consists of a tube divided by a central partition, F B (Fig. 120), terminating at the eyepiece, C, in a knife-edge, which, being inside the range of vision, is not seen when the instrument is in use. At the other end of the instrument are two receptacles, D D, of equal value, alterable in size and shape by means of diaphragms. The two receptacles are here divided by the thick end of the partition, B, which, together with the sides, is recessed by grooves in order to hide the edges of the standard glasses and of the vessels placed in the tube for observation; the top is provided with slots in line with the grooves, which admit and guide the coloured standard glasses into the tubes. A friction rod with clips is fitted on each side to retain the vessels of liquid in position, and the whole is arranged in such a way that the only light which can reach the eye of the observer must first pass in equal quantities through the object in one tube, and the standard glasses in the other.

For measuring colour in opaque objects the instrument is fitted to a hinged stand, capable of being placed at such an angle as reflects the light from the whitened bottom and sides through the tubes to the eye, so that on looking through the eyepiece two white equal fields of view are seen; the object to be measured is placed on the stage under one tube, and the standard glasses worked in the other, against the white back ground. When the colour of two

\* *Journ. Soc. Dyers and Col.*, 1887, p. 186.

objects are to be compared with each other, one is placed under each tube, and standard glasses added to the lightest in colour until both sides are equal, when the difference between them, either in depth of colour or tint, can be read off.

The vessels for holding liquids to be measured are gauged to contain a body of liquid varying in thickness from  $\frac{1}{16}$  in. for dark liquids, up to 2 feet for very pale liquids; with the latter the depth of the blue colour of distilled water can be easily measured. The vessels are made in brass, with colourless glass ends, for neutral and alkaline solutions, and entirely in glass for acids and other corrosive liquids.

When dissimilar substances are to be compared or measured, the intensity of light used becomes an important factor, and extremes cannot be ignored, for whilst there is a considerable range of daylight within which the judgments of the eye are uniform, care is required outside these limits, and practice soon shows at what point the work must be abandoned from insufficient light; and with a light-growing intensity, where the use of modifiers should begin. In matching a given colour, it is found best to make a mental estimation of the primary colours of which the sample is composed, and, if possible, match entirely by means of primaries; but as primaries in glass are at present unattainable, it sometimes becomes necessary to start with the compound standard colour which nearest approaches that under examination, and finish the matching with the primaries in which it may be deficient.

From the description already given, it will be seen that when either a liquid or a solid colour has been matched with the standards, the numbers on

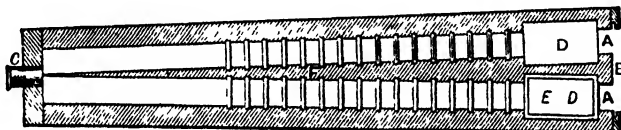


Fig. 120.—Lovibond's tintometer.

the matching glasses afford a complete record of the several colours and tint units of each colour constituting the shade matched. In testing colouring matters, the samples are dissolved in water, alcohol, or other liquid, as the case may require; one of the gauged glass vessels is filled with the solution and placed in position (as shown at E D) on one side of the instrument, and the colour compared either with the standard glasses or with a solution of a standard colour. As previously stated, it is most important that the colour should not be too deep. The best matchings are made with colours equal in depth to 10 or 20 tint-units; if much deeper than this, the solution should either be diluted or a gauged glass of less thickness be employed.

The tintometer will be found of especial value to the colour and extract manufacturer, and wherever colouring matters have to be brought to a given standard of strength or shade.

## INDIGO.

Since the first edition of this work was published many new processes have been brought forward for the analysis and valuation of indigo. Fundamentally, however, the methods now recommended do not differ from those previously given, though modifications ensuring greater accuracy have been introduced.

The value of dyes as a class is ascertained by making comparative dye-trials. It is only in a few cases that methods of chemical analysis are



used. Indigo stands out prominently as one of these exceptions. Unless the colouring matter in a dyestuff can be readily determined with a fair degree of accuracy, the method of valuing by comparative dye-trials is much to be preferred. It should be borne in mind, however, that the experimental error involved in making dye-tests is great in comparison with that of an ordinary chemical analysis. Even under the most favourable conditions, the eye is incapable of discriminating between two shades of the same colour if the difference is less than a certain small amount, which in a chemical analysis would be considered great.

It has often been recommended to test samples of indigo by means of dye-trials in small vats in a similar manner to the dyeing of indigo on a large scale; the zinc or hydrosulphite vat being the one usually recommended. The results, however, are altogether untrustworthy. It is impossible to secure identical conditions in the several small vats employed, and the slightest variation is sufficient to cause a great difference in the depth of shade obtained. Two tests made with the same quantity of the same sample rarely come out the same; very often the difference is great. A much better method of making dye-trials with indigo and one which gives fairly good results, is to dye swatches of woollen cloth or yarn with the indigo disulphonic acid. For this purpose 0.5 grm. of the sample is dissolved in 20 c.c. of concentrated sulphuric acid and diluted with water to 500 c.c. 10 grms. of wool are then dyed with 50 c.c. of solution and compared at the same time with a standard sample. In the *Journal of the Society of Dyers and Colourists* (1897, p. 124), Grossmann gives a description of a special form of apparatus for testing indigo by dye-trials. Fairly good results may be obtained by making colorimetric tests with these solutions, which, however, must be filtered from the dark green insoluble matter usually present. But even after filtering, solutions obtained from various indigos often possess very different shades on account of varying quantities of impurities present, and, when this is the case, it is very difficult to arrive at satisfactory results. This difficulty, however, may be removed by precipitating the colouring matter with salt and redissolving it in distilled water.

The methods employed for testing indigo may be broadly classified into three groups—

1. Conversion into indigo sulphonic acid.

- (a) Indigotin estimated by oxidation.
- (b) Indigotin estimated by reduction.

2. Indigotin reduced in an alkaline solution; the indigotin re-oxidised, separated, purified, and weighed; or dissolved in acid and titrated as in 1.

3. Extraction by volatile solvents

**Preparation of the Sample.**—In the first place it is, of course, important that the composition of the sample taken for analysis should represent as nearly as possible that of the bulk from which it has been obtained. Until dealers and consumers fully appreciate the great importance of accurately sampling chests of indigo they will always be inclined to look upon chemical analysis with a certain amount of distrust. Very often a single piece of indigo is sent for analysis. Sometimes three, four, or five lumps, representing fifteen or twenty chests, are sent. Perhaps after some time another sample from the same bulk is submitted, and the senders express surprise if it does not come out exactly the same as the first one. It is true that in the finer qualities of indigo there is little variation in the cakes or lumps forming a chest, or, indeed, in a string of chests, but in low and medium Kurpahs the variation is often very great. It is frequently possible to pick out from

a chest of indigo pieces varying in colouring matter to the extent of 10 per cent. In order to arrive at an approximate valuation of such chests it is evident that the testing of one or two pieces only is of little or no use. The testing sample is prepared by taking small pieces from each of the lumps in the sample and pounding them together in a mortar. After grinding a portion to a powder, it is passed through a fine sieve, and any particles remaining are returned to the mortar until the whole of the sample will pass through the sieve. It is particularly important that the indigo should be extremely fine when processes in group 2 are employed.

In the *Journal of the Society of Dyers and Colourists*, 1885, pp. 74 and 201, Rawson gives a description of various methods of indigo testing.\* From these papers, and others since published by him, the following processes are, unless otherwise stated, chiefly taken:—

1.- **Dissolving the Indigo in Sulphuric Acid.**—Various methods have been recommended for dissolving the sample in acid, but the following has been found to give the most satisfactory results:—

Half a gramme of finely-powdered indigo is intimately mixed in a small mortar with its own weight of ground glass. The mixture is gradually and carefully added, during constant stirring with a glass rod, to 20 c.c. of concentrated sulphuric acid contained in a cylindrical porcelain crucible (cap. 30 c.c.); the mortar is rinsed out with a little powdered glass, which is added to the contents of the crucible, and the whole is exposed in a water oven for a period of  $\frac{3}{4}$  to 1 hour to a temperature of about 70° C. The sulphindigotic acid thus formed is diluted with water, made up to 500 c.c., and the liquid filtered in order to separate certain insoluble impurities, which would otherwise interfere with subsequent operations.

Bergtheil and Briggs,† for the sake of convenience, prefer Dr. Schulten's method of sulphonation. Instead of open crucibles small glass-stoppered bottles, which can be easily and rapidly shaken, are used. The operation is conducted at the temperature of a briskly boiling water-bath for a quarter of an hour.

Pure indigo blue dissolved in sulphuric acid is, by the action of various oxidising agents, more or less readily converted into a pale yellow body named sulphisatic acid.

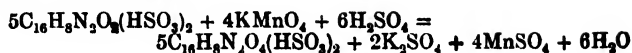
(a) **Potassium Permanganate Method.**—Of all the processes depending upon the oxidation of indigo this is by far the best. It is important (as it is in all other cases) to operate upon very dilute solutions, otherwise the end of the reaction is obscured by the dark colour of the liquid. This fact has been overlooked by previous writers, and has been the cause of bringing the permanganate method, along with other oxidation processes into disrepute.

The following mode of procedure is recommended:—25 c.c. or 50 c.c. of the filtered solution (prepared as above described) are measured into a porcelain dish, to which are added 300 c.c. of distilled water. To this diluted liquid a solution of  $\frac{N}{10}$  permanganate of potash (0.632 gm. per litre) is gradually run in from a burette until the liquid, which at first takes a greenish tint, changes to a light yellow. With indigotin and the better qualities of indigo the end of the reaction is remarkably clear and distinct, and even with an inferior "Kurpah" containing much foreign matter it is easy, with a little practice, to obtain results agreeing very closely one with another.

\* See also Helen Cooley, *Journ. Anal. Chemistry*, vol. ii., p. 129; E. v. Cochenhausen, *Leipziger Monat. für Textil-Industrie*, vol. iii., p. 406; F. Ulzer, *Mitth. des k. k. Technol. Gewerbe-Museums*—abstract in *Journ. Soc. Dyers and Col.*, 1891, p. 183; J. Grossmann, *Journ. Soc. Chem. Ind.*, 1905, p. 308; Bergtheil and Briggs, *Journ. Soc. Chem. Ind.*, 1906, p. 729; *Allen's Commercial Organic Analysis*, as well as the various references mentioned in the text.

† *Journ. Soc. Chem. Ind.*, 1906, p. 729.

According to the equation—



four molecules of potassium permanganate oxidise five molecules of indigotin sulphonic acid, and consequently 316 parts of potassium permanganate become the measure for 655 parts of indigotin. Although with a strong solution of indigotin the theoretical quantity of permanganate is decolourised, yet it has been found, on working with a dilute solution, that the end of the titration is reached by the consumption of a smaller amount of potassium permanganate than is indicated by the above equation. In order to obtain comparative results it is necessary that the solution of indigo should be dilute, in which case the reaction which takes place is not strictly according to the above equation; therefore the strength of the "permanganate" solution should be ascertained by dissolving 0.5 grm. of pure indigotin in sulphuric acid, and treating the solution obtained as previously described. With the dilution given above, each c.c. of  $\frac{N}{10}$  potassium permanganate corresponds to 0.0015 of indigotin. The results obtained by this method are somewhat too high, yet they give one a fairly approximate idea of the relative values of different samples under examination.

With pure indigotin dissolved in sulphuric acid, the action of permanganate is strictly quantitative. The end reaction is clearly defined. Different observers with very little practice obtain precisely the same results. Unfortunately, natural indigo usually contains various other substances which more or less act upon permanganate, but the effect of these substances on the results has been much overrated. If the solutions are sufficiently dilute, and care is taken with the titration, fairly accurate results for commercial purposes are obtained with most classes of indigo. If the indigo contains more than 1 or 2 per cent. of indirubin, the end reaction, instead of being yellow, is orange or scarlet, according to the amount of red colouring matter present. When such is the case, the indirubin must be estimated separately, as given on p. 827.

The *approximate* amount of indigo red may be estimated by continuing the addition of permanganate until the orange or scarlet solution turns yellow. This further addition of permanganate must be made very slowly with constant and violent stirring. In calculating results the same figure is used for indirubin as for indigotin.

*Example.*—(1 c.c. of potassium permanganate = 0.0015 grm. of indigotin.) 1 grm. of "Kurpah" indigo was dissolved in sulphuric acid, diluted to a litre and filtered; 25 c.c. (= 0.025 of indigo) diluted with 250 c.c. of water required 8.3 c.c. of permanganate;

$$\therefore \frac{0.0015 \times 8.3 \times 100}{0.025} = 49.80 \text{ per cent. of indigotin.}$$

If the permanganate solution be strictly  $\frac{N}{10}$  and the above quantities be adhered to, it is merely necessary to multiply the number of c.c. of permanganate consumed by 6.

**Salting-out Method.**—In order to eliminate the error due to the oxidising action of permanganate upon substances other than indigotin, the colouring matter is precipitated by common salt, and the extraneous matter removed by filtration. The 50 c.c. of the filtered solution of indigo, instead of being directly titrated with permanganate, are mixed in a small flask or bottle with 50 c.c. of water and 32 grms. of common salt. The liquid, which is thus almost saturated with salt, is allowed to stand for an hour, when it is filtered, and the precipitate washed with about 50 c.c. of a solution of salt (specific gravity 1.2). The precipitated sodium indigotin sulphonate is dissolved in hot water, the solution

cooled, mixed with 1 c.c. of sulphuric acid, and diluted to 300 c.c. The liquid is then titrated with potassium permanganate as before. It is necessary to make a slight correction in order to allow for the small quantity of sodium indigotin sulphonate which dissolves in a saturated solution of common salt. This correction for the quantities given has been found to be 0.001 gm. If the indigo previous to its solution in sulphuric acid is treated with strong hydrochloric acid, washed well with water, and dried, it is unnecessary to precipitate the colouring matter with salt.

Calculation of results :—

*Example.*—50 c.c. (= 0.05 gm. of indigo) of the indigo solution were mixed with 50 c.c. of water and 32 grms. of common salt. The precipitate was collected on a filter, and dissolved in 300 c.c. of water containing 1 c.c. of sulphuric acid. This solution required 15.2 c.c. of permanganate ;

$$\therefore \frac{(0.0015 \times 15.2 + 0.001) \times 100}{0.05} = 47.60 \text{ per cent. of indigotin.}$$

(b) Barium Chloride Precipitation Process.\*—It has already been mentioned that the sulphuric acid solution of indigo, after making up to a given volume, must be filtered before being titrated. The first portions coming through the filter are rejected, as filter paper absorbs some of the colouring matter. Some qualities of filter paper absorb more than others, and the rate of filtration also causes a difference. Moreover, some of the suspended impurities are in an exceedingly fine state of division, and are liable to pass through many kinds of filter paper, and thus occasion inaccurate results.

The suspended particles subside after long standing, but with some classes of indigo subsidence is not complete after many hours. Various precipitants were tried, and barium chloride was found to give the most satisfactory results. The proportions recommended are as follows:—0.5 gm. indigo is dissolved in sulphuric acid as already described, and, after diluting with water but before making up to 500 c.c., 10 c.c. of a 20 per cent. solution of barium chloride are added. The solution is poured into a bottle, and the barium sulphate formed immediately begins to subside and carries down with it the suspended impurities of the indigo. In fifteen to twenty minutes the requisite amount of perfectly clear solution may be withdrawn by a pipette for titration. By this means not only are the results more concordant but the solution is clearer than when filter paper is used. In fact, the results thus obtained are practically the same as those given by "salting out."

Grossmann† uses calcium carbonate as a precipitant. He claims that certain impurities are thrown down by neutralising the acid solution which otherwise are soluble. 100 c.c. of a solution of 1 gm. of indigo per litre are put into a 500 c.c. flask, to which is added a sufficient quantity (about 6 grms.) of pure calcium carbonate. The flask is filled up to the mark and well shaken. Half of the filtered solution is measured into a porcelain basin, acidulated with sulphuric acid and titrated with permanganate.

Bergtheil and Briggs‡ contend that both barium chloride and calcium carbonate cause a partial precipitation of colouring matter, and, therefore, give results which are too low. Instead of adding barium chloride direct to the indigo solution they mix it with a slight excess of sulphuric acid and then add the indigo solution to the mixture.

Donath and Strasser§ remove the impurities by means of various solvents in a Soxhlet's apparatus, using successively dilute hydrochloric acid, hot water,

\* Rawson, *Journ. Soc. Chem. Ind.*, 1899, p. 251.

† *Ibid.*, 1905, p. 308.

‡ *Ibid.*, 1906, p. 729.

§ *Zeit. f. ang. Chem.*, 1894, p. 49 (*Abs. Journ. Soc. Chem. Ind.*, 1894, p. 426).

and a mixture of alcohol and ether. The residue is dried, dissolved in sulphuric acid, diluted, and an aliquot part titrated with permanganate.

**Tetrasulphonate Process.**—W. P. Bloxam, in the *Journal of the Society of Chemical Industry* (1906, p. 735), adversely criticises several methods of indigo analysis, particularly the permanganate process. He recommends a method which is similar in principle to the "salting out" method above described and finally makes use of a standard solution of potassium permanganate or of titanium chloride. One gm. of indigo is weighed out into a small (1 oz.) spouted beaker. 2 to 3 grms. of purified sand and 5 c.c. of fuming sulphuric acid (25 per cent.  $\text{SO}_3$ ) are added and the mixture stirred with a glass rod. It is heated in the water oven for half an hour and subsequently diluted to 500 c.c. 100 c.c. of this solution are mixed with 80 c.c.\* (in the original paper 100 c.c. were taken) of a solution of potassium acetate containing 450 grms. per litre. A precipitation takes place, but the mixture is warmed until complete solution is attained. The solution is now cooled in a stream of running water and then left for an hour in a vessel containing ice and water. The tetrasulphonate which crystallises out is collected in a Gooch crucible and washed with a solution (ice-cold) containing 225 grms. potassium acetate and  $12\frac{1}{2}$  c.c. of glacial acetic acid per litre. The precipitate is finally dissolved in hot water, the solution cooled and made up to a known volume, and an aliquot portion titrated with potassium permanganate or titanium trichloride.

(c) **Hydrosulphite Method.**—This process, which was recommended by A. Müller,† depends upon the fact that a solution of sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) reduces indigotin-disulphonic acid quantitatively to the corresponding leuco-compound. The apparatus required for this operation is rather elaborate, and considerable care must be exercised in its manipulation; but when all the details are carried out, analyses may be performed in a short space of time, with great accuracy.

The mode of procedure given in the following differs somewhat from Müller's description, but only in a few details:—

**Preparation of Sodium Hydrosulphite.**—100 c.c. of sodium bisulphite (specific gravity 1.38) are mixed in a flask with 200 c.c. of water and 10 grms. of zinc powder, which has previously been worked into a paste with a little water. After about half an hour the liquid will be found to have lost the smell of sulphurous acid. The clear solution is now decanted and well mixed in a flask with about 700 c.c. of water containing, in suspension, 20 grms. of recently slaked lime. The solution of hydrosulphite thus prepared will be about ten times too strong for use. Therefore 100 c.c. of the clear liquid are taken and diluted to a litre in a convenient store bottle, and about 50 c.c. of petroleum oil are poured on the surface of the liquid to prevent oxidation. The bottle is provided with a cork through which pass two tubes, one of which is in the form of a syphon, and is used to fill the burette; the other tube, which only just passes through the cork, is connected with a supply of hydrogen or coal-gas. If one has proceeded correctly the strength of this working solution should be equivalent to about 0.0025 gm. indigotin per c.c., but it requires standardising.

A standard solution of hydrosulphite may also be conveniently prepared by dissolving 3 grms. of hydrosulphite powder of the Badische Anilin- und Soda-Fabrik in a litre of water containing 2 grms. of caustic soda.

**Standardising the Hydrosulphite.**—The solution may be standardised either by pure indigotin, or by an ammoniacal solution of sulphate of copper, using in the latter case a solution of indigo carmine as an indicator. The former method is preferable, and for this purpose 1 gm. of pure indigotin (or a corresponding amount of indigotin of known purity) is dissolved in sulphuric acid, as

\* *Journ. Soc. Chem. Ind.*, 1907, p. 1176.

† *Berl. Berichte*, vol. xiii., p. 2283, and *American Chemist*, vol. v., p. 128.

previously described, and diluted to a litre. 50 c.c. of this solution are measured into a wide-mouthed flask (capacity 200 c.c.), boiled to expel air, and allowed to cool. The flask is provided with a caoutchouc stopper, perforated with three holes, into one of which is fitted a Mohr's burette containing the hydrosulphite solution. The two other apertures serve for the entrance and exit of a current of hydrogen or coal-gas. It is essential that the process should be conducted without access of air. The burette is furnished with a perforated cork, through which passes a glass tube connected with a supply of coal-gas; and at the lower extremity a glass tube is joined to it, which is in connection with the bottle filled with sodium hydrosulphite above mentioned. By this means the burette can be refilled without fear of oxidising the hydrosulphite solution. The flask containing the 50 c.c. of indigotin solution is attached to the caoutchouc stopper, and the air is expelled by a current of coal-gas, which should first pass through U-tubes containing ferrous hydrate. The solution of hydrosulphite is now gradually run in until the solution is just decolourised. The 50 c.c. of indigotin solution are equivalent to 0.05 indigotin, so that if, for example, 20 c.c. of hydrosulphite have been required for the titration, each c.c. of the hydrosulphite will correspond to 0.0025 indigotin. As the hydrosulphite solution is liable to change, it must be restandardised whenever an analysis of indigo is to be made.

**Titration of Solution of Indigo.**—The operation is performed in a similar manner to that just described. 0.5 gm. of indigo is dissolved in sulphuric acid and made up to 500 c.c. in the same way as given above under *Permanganate method*; 50 c.c. are then titrated with hydrosulphite until decolourised.

With indigotin and the better qualities of indigo, the liquid, when fully reduced, becomes of a pale yellow tint, but with inferior samples the solution is more or less of a dirty brownish-yellow colour. In both cases, however, the end of the reaction is quite clear and distinct.

*Example.*—50 c.c. (= 0.05 gm. indigotin) of standard indigo solution required 22.5 c.c. of hydrosulphite;

$$\therefore 1 \text{ c.c. hydrosulphite} = \frac{0.05}{22.5} = 0.00222 \text{ indigotin.}$$

0.5 gm. of Java indigo was dissolved in sulphuric acid and diluted (with addition of barium chloride) to 500 c.c.; 50 c.c. required 16.5 c.c. of hydrosulphite;

$$\therefore \frac{0.00222 \times 16.5 \times 100}{0.05} = 73.26 \text{ per cent. indigotin.}$$

Indigo solutions containing indigo red are acted upon by hydrosulphite in a similar manner as by permanganate. That is to say, the indigo red is not affected until all the indigotin has been decolourised. Indirubin may, therefore, be approximately estimated by this process. In a mixture of the two colouring matters the end of the titration is taken for indigotin when the blue solution turns reddish-violet; the titration must not be continued until a pure red is obtained. The number of cubic centimetres are recorded for indigotin and the titration continued until the red has disappeared. The additional amount of hydrosulphite required being calculated into indirubin.

Gerland \* recommends titration with hydrosulphite and uses the apparatus described by Tiemann and Preuss † for the estimation of oxygen in water. In the first place, by means of sulphuric acid (specific gravity 1.67), he converts the indigotin into monosulphonic acid and removes insoluble impurities by filtration through sand. By the addition of water to the acid solution, indigo-monosulphonic acid is precipitated, which is collected on a filter, washed and dried, and converted into the soluble disulphonic acid by treatment with concentrated sulphuric acid.

\* *Journ. Soc. Chem. Ind.*, 1896, p. 15. † *Berl. Berichte*, 1879, p. 1768.

Binz and Kufferath\* recommend that the titration with hydrosulphite be carried out *in vacuo*. The air in the flask containing the indigo solution to be titrated is displaced by hydrogen and the flask is then exhausted to 14 mm. They find that if indigo is sulphonated at 45° C., or at a lower temperature, the solution requires more hydrosulphite than if sulphonated at 55° C. This is owing to the formation of different sulphonic acids.

**Titanous Chloride Method.**—This method, which has been worked out by Knecht, † is similar in principle to the hydrosulphite process. Titanous chloride has the advantage over hydrosulphite in being much more stable. A standard solution of convenient strength is prepared by boiling together 50 c.c. of commercial titanous chloride (20 per cent. solution) and 50 c.c. strong hydrochloric acid, and then on cooling making up to 2 litres. The bottle containing this standard solution is connected with the burette and the contents are kept under constant hydrogen (or coal-gas) pressure. The solution may be standardised by means of ferric iron. 0.35 gm. ferrous ammonium sulphate is dissolved in 25 c.c. of water, acidulated with dilute sulphuric acid, and oxidised with a dilute solution of potassium permanganate. This solution is then titrated with the titanous chloride solution, as described under *Iron Compounds* (p. 793). 262 parts of indigotin correspond to 112 parts of iron.

The titanous chloride solution may also be standardised by means of a solution of pure indigotin as in the case of hydrosulphite.

In working with commercial natural indigo, Knecht found the impurities to obscure the end reaction, but by following Grossmann's method of purification with calcium carbonate this difficulty was entirely removed and the finish was perfectly sharp and distinct. The operation is carried out as follows:—1 gm. of indigo is sulphonated with 5 c.c. of 100 per cent. sulphuric acid at 90° C. for an hour. The solution is diluted with about 300 c.c. of water and poured into a 500 c.c. flask. 12 grms. of chalk are then slowly added to the warmed solution, and after evolution of CO<sub>2</sub> has ceased, the liquid is cooled and made up to 500 c.c. When the precipitate has completely subsided 50 c.c. are withdrawn and run into a conical flask, to which are added 25 c.c. of a 20 per cent. solution of Rochelle salt. The indigo solution is boiled and the flask then attached to the TiCl<sub>3</sub> burette. The flask is provided with an india-rubber stopper having three holes, one for the introduction of carbon dioxide, a second for the escape of the gas, and the third for the burette tube. After the air has been displaced by CO<sub>2</sub>, the titanous chloride solution is run in until the blue colour changes to yellow.

*Example.*—1 gm. of indigo was sulphonated and diluted to 500 c.c. 50 c.c. required 19.2 c.c. of titanous chloride. 1 c.c. TiCl<sub>3</sub> = 0.001557 gm. Fe;

$$\therefore \frac{0.001557 \times \frac{262}{112} \times 19.2 \times 100}{0.1} = 69.93 \text{ per cent. indigotin.}$$

This method has also been shown to be suitable for indirubin and for Thio-indigo red.

**2. Reduction of Indigotin in Alkaline Solutions.**—Numerous processes have been proposed for estimating indigotin gravimetrically by means of reducing agents. They have all one end in view—viz., the formation of indigo white by the action of nascent hydrogen and its subsequent reoxidation to indigotin. In many cases a considerable loss of indigo takes place, but the following process, based on the principle of the hydrosulphite vat, gives accurate results.

\* *Färb. Zeit.*, 1903, p. 225; *Journ. Soc. Chem. Ind.*, 1903, p. 885.

† *Journ. Soc. Dyers and Col.*, 1904, p. 97; and 1905, p. 292.

*Reduction by Sodium Hydrosulphite and Lime.*—This process, devised by Rawson, is carried out as follows:—1 gm. of finely-powdered indigo is ground into a thin paste with water and introduced into a 40-oz. flask with 500 to 600 c.c. of limewater. The flask is furnished with an india-rubber stopper, which has three perforations, in one of which is inserted a syphon closed by a pinchcock, while in another is fixed a funnel provided with a stopcock. The third aperture serves, by means of a short bent glass tube, for the entrance of a current of hydrogen or coal-gas. The flask is connected with the gas supply, and the contents heated to about 80° C. About 250 c.c. of a solution of sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), about four times as strong as that described on p. 820, are now introduced by means of the funnel, and the mixture, which in a few minutes assumes a yellow tint, is kept near the boiling point for half an hour. After allowing the insoluble matters in the flask to subside, 500 c.c. are syphoned off and the rest of the liquid accurately measured. The 500 c.c. are poured into a conical flask, and, by means of an aspirator, a current of air is drawn through the liquid for about twenty minutes. The excess of hydrosulphite is thus oxidised to sulphite, and the indigo-white to indigotin. Hydrochloric acid is then added, and the liquid heated nearly to boiling. The precipitate is collected upon a previously tared filter, washed with hot dilute hydrochloric acid and then with boiling water, dried at 105° C., and weighed. On account of this precipitate being possibly contaminated with some brown matter it is preferable to collect it upon an asbestos filter, wash well, and dry; dissolve in concentrated sulphuric acid, dilute with water, and titrate an aliquot part with permanganate.

*Example.*—1 gm. of indigo was reduced as above described. The liquid measured 935 c.c. 500 c.c. were oxidised and the precipitate collected upon asbestos. When dry it was dissolved in sulphuric acid and made up to 500 c.c. 25 c.c. required 10·2 c.c.  $\frac{7}{8}$  permanganate.

$$\therefore 0\cdot0015 \times 10 \cdot 2 \times 20 \times \frac{935}{500} \times 100 = 57\cdot22 \text{ per cent. indigotin.}$$

In the *Journal of the American Chemical Society*\* (1885, p. 16), H. M. Rau describes a modification of Fritzsche's method for the analysis of indigo. From 1·5 to 2 grms. of the sample in fine powder are introduced into an 8-oz. Erlenmeyer flask, fitted with a doubly-perforated rubber stopper, through which pass a bent tube provided with a stopcock and reaching just below the stopper, and a second tube of syphon shape reaching nearly to the bottom of the flask. The latter tube terminates in a small funnel, in which a wad of glass wool is placed. From 3 to 4 grms. of pure grape sugar, 15 to 20 c.c. of a 40 per cent. solution of caustic soda, 60 c.c. of water, and about 120 c.c. of 90 per cent. alcohol are added, and the weight of the whole taken. The flask and tubes having been previously weighed alone, a small piece of rubber tubing, closed with a pinchcock, is slipped over the syphon tube, and the flask heated on the water bath for about half an hour. The reduced indigo readily dissolves, the liquid assuming a deep yellow colour. After about an hour the flask is connected with an apparatus generating carbon dioxide, and the liquid syphoned off as far as possible, the wad of glass wool retaining the solid particles. The flask is again weighed, whereby the weight of the liquid run off is obtained. A current of carbon dioxide is passed through the liquid for about fifteen minutes, and afterwards a current of air, which completes the precipitation. The precipitate is collected upon a previously tared filter, washed with hot dilute hydrochloric acid and then with boiling water, dried at 110° C., and weighed.

F. A. Owen† reduces the indigo by a mixture of zinc dust and strong

\* Also *Chem. News*, vol. li., 1885, p. 207.

† *Journ. of Amer. Chem. Soc.*, Nov. 1888; *Chem. News*, vol. lriii., p. 301.



ammonia, reoxidises an aliquot portion of the solution, and weighs the washed and dried precipitate on a tared filter.

**3. Extraction by Volatile Solvents.**—A great number of processes have been devised for estimating indigotin in indigo by means of various volatile solvents.

*By Aniline.*—M. Hoenig\* recommends the following process:—From 0.5 to 0.8 grm. of indigo is mixed with about 2.5 grms. of finely-powdered dry pumicestone, and the mixture introduced into a Zulkowsky-Wolfbauer extraction apparatus. About 50 c.c. of aniline or nitrobenzene (preferably the former) are used for extracting. The operation is said to be completed in an hour, but it is recommended that the mass be removed from the apparatus, washed with alcohol, dried, powdered, and extracted a second time. The solution is afterwards evaporated down to a few c.c. and mixed with five times its volume of absolute alcohol. The precipitated indigotin is collected on a weighed filter, washed with alcohol, dried at 110° C., and weighed. There are several objections to this process. Indigotin is by no means readily extracted by aniline; moreover, other substances of a brown colour are somewhat soluble. Indirubin is not determined since it is removed by the washing with alcohol.

Brandt† also recommends the use of aniline oil, and claims an advantage, inasmuch as he removes the excess of aniline by hydrochloric acid instead of alcohol.

*By Phenol.*—In a later paper‡ Brandt points out that if the extraction with aniline is continued beyond a certain time, indigo is rapidly destroyed. In place of aniline he proposes to use phenol, and gives the following directions:—30 grms. of phenol are taken for about 0.2 grm. indigo. The boiling phenol dissolves the indigotin very rapidly, the extraction being complete in less than half an hour. On cooling, the indigo is precipitated in an amorphous state. 20 grms. dry caustic soda dissolved in about 250 c.c. distilled water are now added to the extract and the contents of the vessel shaken. The solution is then filtered through a tared filter, the precipitate washed with boiling water until the filtrate is neutral, then with alcohol until it passes through colourless, or just tinged blue. The precipitate is dried at 110° C. until a constant weight is obtained.

*By Naphthalene.*—Schneider§ recommends the use of naphthalene, and gives the following details of the process:—

The naphthalene (50 grms.) is boiled in an Erlenmeyer flask, through the cork of which passes a tube 15 millimetres in width and a metre long. In the side of the tube within the flask there is an opening, and the bottom of the tube is contracted and slightly bent. The indigo (0.5 to 1 grm.) is mixed with glass wool, placed in a paper coil surrounded by a linen one, and suspended below the bottom of the tube in the flask, so that the naphthalene falls into the coil. The boiling must be continued until the drops falling from the coil are quite colourless. On cooling, the naphthalene solution of indigotin is decomposed with ether, filtered, and the precipitate washed with ether, dried, and weighed. The correction to be applied for the indigo decomposed and remaining in solution depends on the relative quantities of naphthalene and indigo used, on the duration of the extraction (with 1 grm. of indigo usually 5½ hours), on the manner of heating, and on the possibility of overheating. In order to determine it, the indigotin obtained on the filter should again be extracted with naphthalene under exactly similar conditions, and the loss on again weighing the

\* *Zeitschr. f. angew. Chem.*, 1889, No. 10; *Analyst*, 1889, p. 177.

† *Rev. Gen. des Mat. Colorantes*, 1897, No. 2.

‡ *Rev. Gen. des Mat. Colorantes*, 1898, p. 26; *Journ. Soc. Dyers and Col.*, 1898, p. 34.

§ *Zeit. Anal. Chem.*, 1895; *Journ. Soc. Dyers and Col.*, 1895, p. 194.

indigotin gives the necessary correction. With 50 grms. of commercial white naphthalene, which was not quite pure, the loss of indigotin on heating over wire gauze was 1 to 4 milligrammes, corresponding to a correction of + 0.1 to 0.4 per cent., with 1 grm. of indigo. By using purified naphthalene and heating on an oil bath, the loss would have been less.

Care must be taken to have the apparatus and the indigo completely dry, in order to avoid the danger of explosion.

*By Nitrobenzene.*—Gerland\* has made a study of nitrobenzene as applied to the estimation of indigotin in indigo, and has devised a neat and convenient extraction apparatus for the purpose.

The apparatus consists of a large test tube 40 mm. diameter and 15 to 20 cm. long, clamped in a retort stand above a burner; a brass tube of 7 to 8 mm. inside diameter and about 50 cm. long serves as a reflux condenser. Its lower end is cut obliquely, and has knobs fused to it to secure the wire hook, on which is suspended the filtering tube. This tube is formed of thin glass tubing about 20 mm. diameter and 4 to 4.5 cm. long, both ends slightly enlarged. Over the lower one a piece of fine calico is wired, upon which a few drops of fine paper pulp are placed, this, after drying, forming a serviceable filter. The cloth is protected against the squirtings of the boiling nitrobenzene by a small shield, such as the lid of a porcelain crucible. The upper end is tied with thin wire, which allows it to be connected to the hook of the condensing tube. The latter passes through a glass funnel, the stem of which has been cut off, resting on the top of the test tube. The condensing tube is held in a central position in the test tube by means of a cork, through which it passes loosely, so as to allow it to slide up and down, and which is held in a clamp. Lastly, the condensing tube is connected with an aspirator drawing a gentle current of air through the apparatus during the operation.

The ground sample of indigo is weighed into the filtering tube; this is hooked to the condensing tube, and the latter fastened in its position centrally to the large test tube, so that the filter is about 6 cm. above the bottom of the test tube. The latter is charged with about 25 c.c. of nitrobenzene, the lamp is lighted, and the aspirator set to work. The function of the latter is highly essential. It draws off the vapours of the boiling nitrobenzene, which would otherwise condense on the sides of the test tube, and escape between its mouth and the covering funnel, and conveys the condensed liquor into the filtering tube. It also carries off the steam from the water, which otherwise would condense and fall into the filter tube, causing explosions. By a careful regulation of the aspirator and the heat no nitrobenzene vapours escape into the room, and the test tube is fully supplied with condensed liquor. The vapours of the nitrobenzene do not rise in the tube above 20 cm. With 0.5 grm. of indigo and 25 cm. of nitrobenzene, the extraction requires from one-half to one hour, during which time the aspirator discharges about 2 litres of water. Crystals separate at an early stage, but with regular boiling the operation is not interfered with by bumping. When the droppings from the filter tube are colourless the extraction is complete; the lamp is removed and the apparatus cooled and dismantled.

The indigotin separates in beautiful crystals in a deeply-coloured liquor, and only a very small portion remains in solution. To save the trouble of recovering this, nitrobenzene saturated with indigotin in the cold is used. The liquor is passed through an extracted weighed filter, washed with benzol, and dried. The beautiful appearance of the indigotin thus separated is deceptive. It still contains impurity amounting to from 3 to 6 per cent., and is not fit to be tested by the hydrosulphite method, owing to the deep colouration. A prolonged treatment with hydrochloric acid, or, better still, by hydrochloric

\* *Journ. Soc. Chem. Ind.*, 1896, p. 17; 1897, p. 108.

acid and hydrogen peroxide, leaves it in a pure state fit for weighing or testing with hydrosulphite.

*By Acetic Acid.*—Brylinski\* estimates indigotin by means of boiling glacial acetic acid. The indigo to be examined (about 0.15 gm.) is placed in a thimble filter, the diameter of which is slightly larger than that of the Soxhlet flask, in which the extraction takes place. The best results are obtained by pushing the filter into the extraction tube, not to the bottom, but so that it sticks near the top. A plain tube or air condenser is employed, and the boiling of the acetic acid is effected as briskly as possible by means of a free flame. The extraction is continued until the acetic acid passes through colourless.

After the extraction is completed the flask is allowed to cool, the contents are poured into a beaker and diluted with four times their volume of water. If a small quantity of indigo should remain attached to the walls of the flask, it is dissolved in boiling acetic acid, precipitated with water, and added to the original precipitate. Allowing the liquid now to stand for a few minutes, the precipitate collects in flakes. It is filtered on a tared filter, washed first with boiling water, then with alcohol and with ether, and is finally dried at 110° C. and weighed. Careful washing with alcohol and ether is indispensable since the acetic acid extracts from the corks and from the filter paper (or from the sample) a substance which is partially precipitated by water, but is soluble in alcohol and in ether.

**Other Methods of Analysis.**—Among other methods which do not fall under any of the divisions mentioned on p. 816 the following may be given:—

**Aceto-sulphuric Acid Method.**—Möhlau and Zimmermann† convert indigotin into monosulphate by means of a mixture of acetic and sulphuric acids, then hydrolyse by pouring the filtered solution into water, and weigh the precipitated indigotin as such. 0.1 gm. of the finely-powdered indigo is placed in a 100 c.c. flask with some garnets and 50 c.c. of a mixture of 100 c.c. glacial acetic acid and 4 c.c. sulphuric acid are added. The flask is heated for fifteen minutes on a water bath and the contents filtered hot through a toughened filter paper into a flask of 300 c.c. capacity. The filter is washed with the warm acid mixture until the filtrate is colourless. The filtered solution is heated to 70° C. and then poured very slowly (at first drop by drop) into 100 c.c. of boiling water. When quite cold the liquid is filtered through a tared Neubauer platinum crucible (or a tared toughened filter). The precipitate is washed first with hot dilute hydrochloric acid, then hot water, and finally alcohol, dried at 105°, and weighed as indigotin.

For many reasons the process is not one that would commend itself for commercial purposes. In dealing with natural indigo, Bergtheil and Briggs‡ found that the operations of sulphate formation and hydrolysis had to be repeated many times before pure indigotin was obtainable.

**Sublimation.**—According to C. T. Lee§ indigotin may be conveniently estimated by sublimation. He uses for this purpose shallow platinum trays, 7 cm. long, 2 cm. wide, and 3 to 4 mm. deep. About 0.25 gm. of finely-powdered indigo, which has been previously dried at 100°, is weighed into the tray and spread in an even layer over its surface. The operation is conducted on an iron plate, which is heated gradually to avoid burning. When the surface of the indigo is covered with a shining mass of crystals, a piece of sheet iron, bent into the form of a low flat arch, is placed over the platinum tray, and, at the same time, as the temperature rapidly rises, the gas is turned

\* *Rev. gen. des Mat. Colorantes*, 1898, p. 52; *Journ. Soc. Dyers and Col.*, 1898, p. 75.

† *Zeit. Farb. Tex. Chem.*, 1903, x., p. 189.

‡ *Journ. Soc. Chem. Ind.*, 1906, p. 729.

§ *Chem News*, August, 1884; abstract from the *Journ. Amer. Chem. Soc.*

down. The vapours of indigotin are now given off, and the heat is gradually raised; but care must be taken, lest any yellowish vapours appear, which would indicate the evolution of bodies other than indigotin. When all the crystals of indigotin have disappeared from the surface of the residue, the tray with its contents is cooled in a desiccator and weighed. The loss in weight is indigotin. Unfortunately, the process is not a reliable one. On the one hand, substances other than indigotin may be volatilised, and on the other, indigotin itself partially decomposes, leaving a dark brown residue.

**Nitrogen Determination.**—F. Voeller\* analyses indigo by estimating the nitrogen which a weighed sample contains after purification. The indigo is placed in a perforated platinum crucible closed with asbestos, and with the aid of a filter pump washed successively with hydrochloric acid, soda, alcohol, and hot water. The nitrogen in the residue is then estimated by Kjeldahl's method. The nitrogen found multiplied by the factor 9.36 gives the indigotin. An analysis of commercial indigo quoted by Voeller gave 75.76 per cent. of indigotin, 16.35 per cent. of mineral matter, and 6.48 per cent. of water. But commercial indigo containing so much mineral matter and water *never* contains such a high percentage of indigotin. It is not possible to completely remove certain nitrogenous impurities from natural indigo by the aid of solvents, and this method is, therefore, unreliable.

**Indigo Rich in Indirubin.**—A considerable amount of natural indigo now on the market contains a large proportion of indirubin, whereas formerly this constituent was only present to the extent of 1 or 2 per cent.† It has already been stated under the "Permanganate process" that indirubin may be approximately determined by permanganate, owing to the fact that indigotin is completely oxidised before indirubin is affected when a mixture of their sulphonic acids is titrated by that reagent. The operation, however, requires great practice, and in the presence of impurities the end reaction is not very distinct. When small quantities of indirubin are present in an indigo the following colorimetric process can be recommended:—From 0.1 to 0.25 gm. of the finely-powdered sample is boiled with about 150 c.c. of ether for half an hour in a flask attached to an inverted condenser. When cold, the solution is made up to 200 c.c. with ether and mixed with 10 c.c. of water in a bottle. Shaking up with a little water causes the suspended particles of indigo to settle immediately, and a clear solution of indirubin is at once obtained without filtering. A measured quantity of the solution is withdrawn and compared in a colorimeter with a standard solution of indirubin.

Koppeschaar ‡ extracts the indigo with glacial acetic acid which dissolves indirubin and indigo brown. The latter is removed by treatment with caustic soda which precipitates the indirubin, and this is again dissolved in glacial acetic acid and estimated colorimetrically against a standard.

Gardner and Denton § have tried a number of solvents for indirubin and have found *acetone* to be much the most satisfactory. For the estimation of indirubin they have devised the following process:—0.2 gm. of the finely-powdered and dried sample is placed in a flask and boiled for half an hour with 100 c.c. acetone, with reflux condenser. After cooling, the solution is made up to exactly 100 c.c. with acetone, and then to 200 c.c. with 10 per cent. salt solution. The addition of salt precipitates the small amount of indigotin which dissolves, and also indigo brown and other impurities. After shaking, the solution is allowed to stand for five minutes, filtered, and the indirubin estimated colorimetrically by comparison with a standard solution of indirubin

\* *Zeitschr. f. angew. Chem.*, 1891, p. 110; *Journ. Soc. Chem. Ind.*, 1891, p. 488.

† *Journ. Soc. Chem. Ind.*, 1899, p. 252.

‡ *Zeit. für Anal. Chem.*, 1899, p. 1; *Journ. Soc. Dyers and Col.*, 1899, p. 136.

§ *Journ. Soc. Dyers and Col.*, 1901, p. 170.

prepared with acetone and salt solution in the same way as that of the sample.

**Yellow Colouring Matter in Indigo.**—It has already been stated (p. 312) that Java indigo and indigo made from Natal-Java plant is liable to contain a yellow compound which interferes with the ordinary methods of estimating indigotin. Its presence may readily be detected by the addition of a solution of caustic soda or ammonia to the powdered indigo placed in a porcelain basin or on a filter paper. If present, the alkali immediately produces a deep yellow colour. When this occurs the weighed amount of indigo to be tested should be heated, either with a dilute solution of ammonia or with alcohol, and poured on to an asbestos filter, washed and dried, and then dissolved in sulphuric acid for further treatment. Boiling alcohol is preferable for this purpose, since alkaline solutions containing indigo in suspension are difficult to filter, and under certain conditions indigo enters into solution.

According to Gardner and Denton,\* the yellow colouring matter is soluble in acetone, and this reagent might also be used for removing it from samples of indigo to be tested.

**Water in Indigo.**—In testing indigo it is very important that the amount of water (moisture) present should be taken into consideration, although this factor is generally overlooked. Indigo, both in lumps and in the powdered state, is very liable to change in weight, either drying or absorbing water from the air according to the atmospheric conditions. This property is often the cause of apparent discrepancies in testing. A sample of indigo representing a chest or a number of chests may frequently be found to contain 5 per cent. less moisture than the bulk. Afterward, on delivery of the chests, tests for indigotin are made, and the results naturally come out lower. The indigo is said to be of inferior quality, although the difference may be due entirely to a difference in "condition" or amount of moisture present.

In order to show more clearly the possible variations in the percentage of colouring matter in samples presumably the same, a number of indigos were exposed under different atmospheric conditions.† Two samples of Bengal, two of Kurpah, one of West African, and one mixed lot were taken. The experiments were made in two series—series A in lumps and series B in powder. The indigo was kept for a period of seven days in a room with the temperature averaging 72° F. and the humidity 53. The air was moderately still. The samples were then taken into a cool damp cellar, where the temperature averaged 45° to 46° F., and the air was saturated with moisture. They were afterwards exposed in a draught cupboard to a gentle current of air; the temperature was maintained at 85° F. and the humidity averaged 68.

It was found that a damp Kurpah, containing originally 11.25 per cent. of water, lost upwards of 6 per cent. in seven days at 72° F. in the lump form. In the powder, a loss of 6 per cent. was observed in three days. At a temperature of 85° F., in a gentle current of air, the loss, as was to be expected, was much more rapid; most of the samples, even in the lump form, losing about 6 per cent. in two days. The experiments further showed that dry indigo exposed in a cool damp place was capable of absorbing from 4 to 5 per cent. of moisture in the course of about a week.

The amount of water in indigo is readily determined by heating 1 grm. of the powdered sample to a temperature of 105° to 110° C. in an air-oven for about an hour, cooling in the desiccator and re-weighing. For this kind of determination watch-glasses are usually recommended, but when a number of samples are to be tested it is more convenient to use small beakers about an inch high.

\* *Journ. Soc. Dyers and Col.*, 1901, p. 170.

† *Rawson, Journ. Soc. Dyers and Col.*, 1896, p. 82.

**Ash or Mineral Matter in Indigo.**—It is frequently desirable to estimate the amount of ash in indigo. For this purpose 1 grm. is weighed into a platinum capsule or crucible and ignited over a Bunsen burner, fitted with a rose. At first the flame should be very low, just sufficient to volatilise the indigotin, and throughout the whole operation the heat should not be very great. Some samples are very difficult to burn off completely over a Bunsen. It is preferable to use a muffle furnace at a low red heat, when a number of samples are to be operated upon at the same time.

**Indigo Extract.**—The value of indigo extract may be determined by any of the methods given under Section I., *Indigo*, "where the indigo is dissolved by sulphuric acid." The "barium chloride" or "barium sulphate" method is the most suitable. About 10 grms. of extract are dissolved in a litre of water; and 50 to 100 c.c. of the solution titrated in the presence of sulphuric acid with  $\frac{N}{10}$  permanganate, as previously described.

Comparative dye-tests are especially valuable for indicating the purity of shade. Samples of extract of indigo vary very much in this respect. The tests are best made on worsted yarn or cloth; about 5 per cent. of "extract" and 5 per cent. of sulphuric acid are convenient quantities. *Refined* indigo extract should dissolve completely in water, leaving no green or greenish-grey residue. Common indigo extract contains more or less dirty green insoluble substances.

**Estimation of Free Acid.**—There are "acid" indigo extracts and "neutral" indigo extracts, but the latter, as sold, frequently also contain more or less free acid. The amount of free acid may be readily determined by precipitating the colouring matter with pure salt. For this purpose 100 c.c. of a 1 per cent. solution of the extract is treated with 32 grms. of neutral sodium chloride, and, after standing an hour, with occasional shaking, filtered, and the precipitate washed with a little saturated solution of salt. The filtrate, which is slightly coloured (but this does not interfere with the reaction), is titrated with  $\frac{N}{10}$  caustic soda and phenolphthalein. With a little practice, fairly good results may be obtained by titrating direct without resorting to precipitation.

**Adulteration.**—Samples of indigo extract frequently contain *Soluble blue* and similar coal-tar blues. These may be usually detected by dyeing a skein of silk in an acidified solution of the sample, washing, and boiling in a large volume of fresh water. When this is repeated two or three times, almost the whole of the indigo extract is removed, and the Aniline blue remains on the fibre. The presence of Soluble blue is also indicated by the action of potassium permanganate on a solution of the sample. With pure indigo extract the solution becomes yellow; whereas, if Aniline blue is present, it changes to a lighter blue, violet, or grey. After destroying the indigo by permanganate, a small piece of wool or silk may be dyed in the solution, and the colour recognised on the fibre by special tests.

## LOGWOOD.

Since logwood contains a variable amount of coloured extractive substances other than colouring matter, it is evidently impossible to estimate the amount of the latter by any process based upon the colour of the logwood decoction obtained by boiling with water.

The most reliable method of determining the value of samples of logwood, or logwood extracts, is by means of comparative dye-trials, carried out under the exact conditions under which the dye is to be practically employed. It is essential that strict attention is paid to the latter point, because the practical value of any sample depends largely upon the process used in applying it. For

instance, in the case of two samples of wood containing the same total amount of colouring matter, the latter may consist in one sample of hæmatoxylin, and in the other of hæmatein, and, if dyed on an oxidising mordant (*e.g.*, chromic acid), the former would give a much superior (brighter) colour, whereas, on a non-oxidising mordant (*e.g.*, chromium fluoride), the latter would give much the best result.

The *practical* value for a particular purpose, represented by the *condition* of the colouring matter, may thus be very different from the *theoretical* value, as measured by the *total amount* of colouring matter present. For general purposes the following mode of procedure can be recommended:—

Worsted yarn, slubbing, or cloth (in lots of 10 grms. each) is mordanted with 3 per cent. of bichromate of potash and 6 per cent. of tartar. After well washing, each lot of material is dyed in a separate bath with from 5 to 10 per cent. of the logwood samples to be examined. If logwood extracts are being tested, from 2 to 5 per cent. will be found sufficient. The dye-trials are, of course, made simultaneously, and this is best effected in one of the forms of apparatus previously described. If the samples of logwood be finely rasped, the requisite amount may be carefully weighed out on the balance, and introduced direct into the dye-baths, which must then be boiled for about ten minutes before immersing the material to be dyed. In the case of chipped logwood, however, since for 10 grms. of wool 10 per cent. only represents 1 gm., it would be almost impossible to obtain a fair average in this way. In order, therefore, to overcome this difficulty, the chipped wood must be reduced to powder, but this cannot be accomplished without previously drying the wood. About 50 to 100 grms. of each sample are dried in a water-bath, and then ground to a fine powder in a small coffee mill. In the meantime the percentage of water is estimated in 10 grms. of each sample, so as to be able to calculate the amount of dried powder equal to 1 gm. (or 0.5 gm. as required) of the original wood. If, for example, a sample is found to contain 40 per cent. of water, 100 parts correspond to 60 parts of dry wood. Consequently 0.6 gm. of the dried powder would be equal to 1 gm. of the original sample, the amount required for 10 per cent.

Unless the prepared sample be dried immediately before weighing, it will be necessary to estimate the amount of water it has absorbed during the process of grinding and sampling. Perfectly dry logwood, when exposed to the air, quickly absorbs 5 or 6 per cent. of water.

Another method of obtaining an average sample of chipped logwood is to make an alcoholic solution of the colouring matter. From 10 to 20 grms. of the sample are introduced into a large flask fitted with a cork and long glass tube (or the flask may be attached to an inverted condenser), 500 to 600 c.c. of alcohol (redistilled methylated spirit answers the purpose) are added, and boiled for about a quarter of an hour. The alcoholic solution is poured off into a litre flask, and the residue boiled up again with 300 or 400 c.c. of fresh alcohol. The solution, when cold, is finally made up to 1 litre. If 20 grms. of logwood were weighed out, 50 c.c. of the alcoholic solution correspond to 1 gm.

In some cases it is desirable to ascertain the condition in which the colouring matter principally exists in a sample of logwood. Two series of dye-tests should be made; in one case upon wool mordanted chiefly with chromic acid (say 3 per cent. of potassium bichromate and 1 per cent. of sulphuric acid), and in the other upon wool mordanted with chromium oxide (see p. 339). It will frequently be found that under these conditions two samples of logwood give very different results. A sample of freshly cut wood where the colouring matter exists principally as hæmatoxylin will give superior results on "yellow" mordanted wool, whereas matured logwood containing principally hæmatein will give better results on "green" mordanted wool.

In the case of extracts of logwood, it is advisable to weigh out 10 grms. and dilute with water to 1 litre. The requisite amount for the dye-trials may then be measured. Every 10 c.c. of such a solution corresponds to 1 per cent. when 10 grms. of material are to be dyed.

Several colorimetric processes have been proposed for valuing logwood and its extracts, but they are not nearly so reliable as carefully conducted dye-trials. Perhaps the best method consists in comparing dilute alcoholic solutions of the colouring matter developed by a solution of alum.

Rawson has obtained fairly good results by working in the following manner:—10 grms. of the sample of logwood (or an equivalent amount of extract) are extracted by alcohol, and made up to 1 litre; 10 c.c. of this solution are further diluted with alcohol to 100 c.c. Then 5 c.c. of the dilute solution are put into a Nessler glass (or colorimeter tube), to which are added 5 c.c. of a 1 per cent. solution of alum, and the tube filled to the mark with distilled water. The colour produced (which develops gradually) is compared with a standard sample treated in exactly the same manner. The value of the two samples is in inverse ratio to the number of cubic centimetres required to produce the same depth of tint. If the wood be finely ground, 1 gm. may be taken and made up to 1 litre without further dilution.

H. Trimble\* recommends the following process for testing logwood extracts:—A solution of a standard extract is made of such a strength that 1 c.c. shall contain 0.001 gm. of the dry extract. It is, therefore, first necessary to dry a portion of the sample at 110° C., in order to make the calculation for this solution. Then 1 c.c. of the solution is mixed in a test-tube with 1 c.c. of a solution of copper sulphate (containing 0.002 gm.  $\text{CuSO}_4$ ,  $5\text{H}_2\text{O}$  per c.c.) and 10 c.c. of water, containing in solution a little calcium carbonate. The mixture is quickly heated to the boiling point, poured immediately into a 100 c.c. cylinder, and diluted with distilled water to the mark. The sample of extract to be tested is subjected to the same treatment, and diluted with distilled water until the depth of colour is exactly the same as in the standard, when, on reading off the height of liquid, the comparative value will be known. It is necessary to renew the standard every ten to fifteen minutes, as it fades in that time. Although not stated in the communication, it is obvious, from the description, that the observation is made in the transverse direction of the cylinders, and not through the *depth* of the liquid, which is the usual plan.

During the process of ageing of logwood the ground wood is sometimes sprinkled with an alkali, such as limewater, stale urine, or dilute solution of carbonate of soda. This addition, which must be pronounced fraudulent, gives a temporary bloom to the wood, and causes it to give up its colouring matter to water much more readily. But the colour is much less permanent in the presence of an alkali. If an alkali be present in logwood, the colouring matter will dissolve in distilled water with a violet colour instead of yellowish-orange.

The value of chipped and rasped logwood of the same quality varies to a very considerable extent according to the percentage of water which is present. This may be said to range from 32 to 50 per cent. From 38 to 40 per cent. may be taken as a fair average. If the water exceeds 42 per cent., the logwood, as a rule, may be moulded into compact balls. In order to determine the amount of water, 10 grms. are dried in the water-oven, or preferably at 105° C. in an air-bath, until they cease to lose weight. From two to three hours are required to complete the operation. If necessary, after drying, the ash may be determined by ignition at a low red heat. It should not amount to more than 2 per cent.

\* *Journ. Soc. Dyers and Col.*, 1885, p. 92.



In the case of logwood extracts, not only is the degree of oxidation of the colouring matter very variable, but their value may be largely influenced by the presence of the impurities. Admixture with such bodies as *bark extract, molasses, glucose, dextrin, tannin extracts, &c.*, is largely practised, and is by no means easy of detection. Inorganic adulterants, such as salt, sodium sulphate, or chalk, are also of frequent occurrence, but the detection and estimation of these offer no difficulties. Even in the case of unadulterated extracts a mere determination of the specific gravity gives no indication of the amount of the colouring matter present, on account of the variable amount of other extractive matters which may be present.

The nature of the impurities may have an important influence upon the suitability of any sample for a special purpose. Thus an extract to which 20 per cent. of chestnut extract has been added would be much inferior for wool dyeing to one containing an equal amount of colouring matter reduced with 20 per cent. molasses, because tanning matters tend to give the wool a harsh unpleasant feel, and are thus injurious. For use in the black dyeing of cotton, however, the two extracts would be reversed in value, because the tannin, combining with the iron used as mordant, would help to intensify the black.

A perfectly satisfactory method of analysis should, therefore, indicate the following points:—

(1) Amount of hæmatoxylin; (2) amount of hæmatein; (3) character and approximate amount of impurities.

There is, however, at present no analytical method in vogue which satisfactorily determines these points, and the most reliable results are obtained by carefully conducted comparative dye-trials made under the conditions of practical work.

Zubelin\* proceeds as follows:—Standard solutions are prepared containing 5 grms. extract 51° Tw. per litre having the following composition:—

- (1) Colouring matter entirely unoxidised (hæmatoxylin).
- (2) Colouring matter entirely oxidised (hæmatein).
- (3) Equal parts of hæmatoxylin and hæmatein.
- (4) Four grms. hæmatoxylin paste and 1 grm. sumach.
- (5) Same as No. 1, mixed with 0.5 per cent. chalk.

With these various solutions dye-baths are made up containing 40 c.c. of the solution and 400 c.c. distilled water, and in each 10 grms. of wool previously mordanted with 3 per cent. bichromate of potash and 3 per cent. tartaric acid are dyed.

The results obtained will be as follows:—

- (1) Bright bluish colour.
- (2) Much deeper than 1, approaching black.
- (3) Colour intermediate between 1 and 2.
- (4) Paler than 1.
- (5) About equal to 3.

A similar piece of wool is dyed at the same time with solutions of the extracts under examination made up to the same strength as the standard extracts—viz., 5 grms. 51° Tw. per litre—and the colours thus obtained are compared with the above. It is thus easy to determine when the extracts are partially or completely oxidised. An oxidised adulterated extract may, however, give a similar colour to an unoxidised pure extract, and the following further trials are therefore necessary:—

\* *Bull. Soc. Ind. Mulhouse*, 1898, p. 257.

Wool is mordanted with—

10 per cent.	alum.	
2½	„	potassium bichromate.
2½	„	copper sulphate.
2½	„	tartaric acid.

Patterns thus mordanted are dyed as before, but using only 20 c.c. of the various extracts and 400 c.c. water. The results obtained are very different to those in the first set of experiments :—

- (1) Deep blue.
- (2) Grey, and much paler than 1, 3, 4, or 5.
- (3) Duller than 1.
- (4) Similar to 1, but somewhat paler.
- (5) Similar to 3.

In the case of the two extracts which may appear similar in the first set of experiments, but which differ in that one is an unoxidised extract and the other an adulterated oxidised extract, very different results will be obtained on this composite mordant, the pure unoxidised extract giving much the deeper and brighter colour.

By making additional experiments on cotton, further information or corroboration regarding the degree of oxidation of the samples may be obtained, as will be seen from the following notes :—

Additional standard solutions are prepared as follows :—

- (6) As 1.
- (7) As 2.
- (8) As 2, diluted 20 per cent.
- (9) As 4.
- (10) As 4, with enough chalk to neutralise the tannic acid.
- (11) As 5.

Cotton hanks are dyed in solutions containing 100 c.c. of these extracts diluted to 400 c.c., commencing at 60° to 70° C., and allowing gradually to cool during 1½ hours. After being well shaken out, each hank is immersed for five minutes in a bath containing 3 per cent. of copper sulphate.

The dyed patterns exhibit the following appearances :—

- (6) Light grey.
- (7) Blue-black.
- (8) Between 6 and 7.
- (9) Poor light dull colour.
- (10) Darker than 9, but paler than 8.
- (11) Darker than 6, but paler than 7 and 8.

The reason for the poor results obtained in (9) is that hæmatein is not well attracted by cotton in presence of tannic acid in solution. Extracts containing tannic acid may be further recognised by the peculiar reddish-grey shade they produce.

Methods for detecting and estimating various impurities in logwood extract are given by L. Bruehl in the *Journal of the Society of Dyers and Colourists*, 1889, pp. 111, 122.

## FUSTIC, QUERCITRON BARK, &amp;c.

Comparative dye-tests are made either upon cotton or wool. In the latter case the material is mordanted with 3 per cent. of bichromate of potash, well washed, and dyed in fresh baths with from 20 to 30 per cent. of the yellow woods. In testing extracts 3 to 5 per cent. are convenient quantities. 10 grms. of the extract are made up with water to a litre, and an aliquot part taken for each test. The bottle or flask containing the diluted extract must be well shaken immediately before measuring the required amount. Dye-tests should also be made upon material mordanted with 4 per cent. of stannous chloride and 4 per cent. of tartar. Extracts of fustic, quercitron bark, &c., according to the mode of preparation, vary considerably in shade. Some varieties produce upon "chromed" wool greenish-yellows, while others give brown or orange-yellows. The green shade is generally considered the more valuable, and in making dye-tests this must be taken into consideration. A "red" shade may appear to be deeper and fuller than a "green" shade, when in reality it may contain much less colouring matter. The dyed swatches, after being dried, must be compared by looking "overhand" in various positions, when the *depth* of yellow can be much more accurately discerned. In any case, however, yellow shades, especially if not of exactly the same tone, are difficult to accurately estimate by the eye, and it is far better to combine the yellow with some blue colouring matter so as to produce a green. With samples of fustic, &c., good results are obtained by adding 2 per cent. of logwood extract to each bath. A better method, however, is to make the tests upon material which has been previously dyed a light uniform shade of blue in the indigo-vat. In this way a very small difference in the "yellow" samples is perceived. If a *green* shade of fustic is being compared with a very *red* shade, a small quantity of red colouring matter (such as Alizarin red) should be added to the bath containing the former, and the amount taken into consideration in calculating the value of the samples.

Fustic Extract is liable to contain dextrin, molasses, zinc sulphate, glycerin, alum, turmeric, Aniline yellows, &c. Methods for detecting these bodies are given by L. Bruehl in the *Journal of the Society of Dyers and Colourists*, 1889, p. 124, of which article the following is an abstract:—

*Zinc sulphate* is determined by drying the extract, then gently charring and extracting the finely-powdered mass with dilute boiling nitric acid. The solution is then tested for zinc.

*Alum* may also be tested for in the nitric acid solution.

The presence of *turmeric* is indicated if well scoured unmordanted wool is dyed yellow when boiled with a solution of the sample. Certain aniline dye-stuffs may, however, be present, and special tests must be applied.

*Extract of quercitron* does not dye wool directly, and alum is but a feeble mordant for quercitron upon wool, producing only a poor shade, whilst fustic under similar conditions gives a deep yellow colour. Stannous chloride in the presence of tartaric, oxalic, or hydrochloric acid, dyes in combination with quercitron a deep orange upon wool, while fustic gives delicate shades. On these facts the following methods of detecting quercitron is based:—

A slip of white woollen cashmere, 10 cm. by 20 cm., dyed in a mixture of 0.5 gm. extract, 0.2 gm. alum, 0.5 gm. stannous chloride, 0.5 gm. oxalic acid in 1 litre water, if contrasted with a similar dyeing trial with an extract adulterated with quercitron, will give different results, which difference manifests itself by the greater intensity of colour of the adulterated extract. If now a swatch of the same size is dyed in the extracts under comparison, but with alum mordant alone, the adulterated extract will give weaker colourings than the pure extract of fustic. Although this method does not yield

quantitative results, with some practice the percentage can be determined approximately.

Moritanic acid, or maclurin, has the decided character of a tannic acid, therefore extracts of fustic give all the reactions peculiar to tannic acids.

*Determination of the Amount of Colouring Matter in Fustic Extract.*—10 grms. of the extract, dried at 110° C., are extracted, with absolute alcohol; the remaining insoluble matter consists of extractive substances which contaminate the extract. The alcoholic solution is mixed with three-quarters its volume of hot water, whereby the morin is nearly completely precipitated. The precipitate is washed several times with hot water, and the washing water added to the filtrate. On evaporating the latter to one-half its volume a large quantity of the maclurin separates out, and the remainder on the addition of hydrochloric acid. The total weight of morin and maclurin thus obtained, after drying at 100° C., constitutes the percentage of dyestuff contained in the extract. The method is sufficiently correct for technical purposes.

### TURMERIC.

Comparative dye-tests made either upon wool or cotton give the best results. About 10 per cent. of each sample is taken and dyed with 5 per cent. of alum in a single bath. The value of samples of turmeric may also be obtained by a colorimetric method applied in the following manner:—0.5 gm. is boiled with about 200 c.c. of alcohol for a quarter of an hour, and when cold made up to 250 c.c. 5 c.c. of the filtered solution are run into a Nessler tube, and made up to 100 c.c. with water containing a small quantity of caustic soda.

Powdered turmeric is sometimes adulterated with mineral matter, especially common salt. This may be readily detected by boiling with nitric acid and adding silver nitrate to the solution. The amount is determined by igniting 1 gm. in a platinum crucible, dissolving the ash in water, and titrating the solution with decinormal silver nitrate (p. 754). Good turmeric does not leave more than 5 per cent. of mineral matter.

### THE RED WOODS.

Peach Wood, Brazil Wood, Sapan Wood, &c., and their extracts, may be examined in the same manner as logwood. Comparative dye-tests are made by mordanting wool with 3 per cent. of potassium bichromate, and dyeing in fresh baths with about 20 per cent. of the ground woods, or from 2 to 5 per cent. of extracts. Good results are also obtained by mordanting with 8 per cent. of alum and 8 per cent. of tartar. The dye-tests may also conveniently be made upon calico mordanted in stripes with alumina, iron, and chromium respectively. The commercial extracts, which usually have a density of from 5° to 20° Tw., are liable to contain common salt, which, however, may readily be detected by boiling with nitric acid and adding silver nitrate. The rasped woods should not contain more than about 30 per cent. of water.

Camwood, Barwood, and Saunders-wood are best examined in the following manner:—Wool is mordanted with 2 per cent. of bichromate of potash, and then boiled with 10 to 20 per cent. of the dyewood for an hour. It is squeezed (not washed) and worked in the mordant bath again for about half an hour. Before entering the wool into the dye-bath, the wood should be boiled for fifteen minutes. A second lot of yarn or cloth should be dyed in the bath without any further addition, since one sample may give up its colouring matter much more slowly than another.

## M A D D E R.

For determining the comparative value of samples of madder and madder preparations, dye-trials are made either upon wool or cotton. Since madder is now almost exclusively used in wool dyeing, dye-tests on wool are of the greater importance. The tests should be made upon cloth, mordanted in one case with 3 per cent. of bichromate of potash, and in a second case mordanted with 8 per cent. of alum and 8 per cent. of tartar. The dyeing should be performed in fresh baths, using 30 per cent. of madder, or an equivalent amount of extract, the value of the samples being in the inverse ratio of the amount of material necessary to produce the same depth of shade.

When madder was used in Turkey-red dyeing, the following process was usually carried out:—Equal weights (5 or 10 grms.) of cotton, mordanted in stripes, with alumina and iron mordants, were placed in separate dye-vessels, heated by one large copper bath in the manner already described (p. 811). Equal weights (about 5 grms.) of the samples of madder were added to the various dye-pots, and the temperature gradually raised to 75° C. during the course of 1½ hours, and then heated for 1½ hours further at or near the boiling point. The pieces were then taken out, washed, and compared, and a second series of tests made with quantities of madder judged sufficient to produce the same depth of shade in each case. The total colouring power of the samples was thus obtained, but a further operation was deemed necessary. The dyed swatches were cut into two parts, and one of each was submitted to a treatment in weak soap solution for half an hour, at a temperature of 70° C. The swatches were then washed, dried, and compared with each other, and with the swatches which had not been soaped.

The method of testing Alizarin at the present day is practically the same; much smaller quantities of colouring matter being, of course, taken.

Madder has been found adulterated with a great many substances, both of organic and inorganic origin. Of mineral matters, powdered brick, yellow ochre, sand, and clay have been found; while the organic impurities comprise such bodies as sawdust and ground red and yellow woods.

An adulteration with mineral substances is usually easily ascertained by incinerating a weighed amount in a platinum crucible. Good madder should not leave more than 5 to 10 per cent. of ash, whereas adulterated samples may leave very much more. Some of the mineral substances used for adulteration may also be detected by shaking up the madder with water, and, after allowing the mixture to stand for a short time, pouring off the turbid liquid. The madder remains suspended in the water, whereas the mineral substances quickly subside. By repeating the operation two or three times, the impurities may be obtained free from madder, and can then, if necessary, be further examined.

Persoz devised a very simple method for ascertaining the presence of ground dyewoods, &c., in madder. A piece of filter paper is immersed in a weak solution of stannic chloride, and a similar piece in a solution of ferric sulphate. The test papers are then separately placed on glass plates, and a little of the madder sprinkled over them. After a short time (a quarter of an hour or so) the papers are examined. The possible adulterations of madder produce the following effects:—

*Stannic Chloride Paper.*

Brazil wood, peach wood, &c.,	. . .	crimson-red.
Logwood,	. . .	purple.
Fustic, quercitron, &c.,	. . .	deep yellow.
Madder,	. . .	very faint yellow.

*Ferric Sulphate Paper.*

Logwood, . . . . .	violet-black.
Tannin matters, . . . . .	deep greenish-black,
Madder, . . . . .	very light brown.

Schlumberger estimates the amount of pure colouring matter in madder as follows:—10 grms. of madder are treated with 500 c.c. of water acidulated with acetic acid at 30° C. for 24 hours, and then filtered and washed. The residue is boiled ten minutes with a litre of dilute acetic acid (sp. gr. 1·005) and filtered. The residue is again boiled with a fresh quantity of the same acid and filtered. The solutions on cooling deposit the colouring matter in orange-coloured flakes; some, however, remains in solution, and is precipitated by adding common salt. The precipitate is collected on a small tared filter, washed, dried, and weighed. Schlumberger found by this method from 4 to 4·2 per cent. of colouring matter in good Avignon and Alsace madders. Inferior qualities gave from 1·9 to 2·7 per cent. only.

## CUDBEAR AND ORCHIL.

The colouring principles in these bodies being practically the same, they may be examined by the same processes. In order to determine the value of a number of samples, comparative dye-trials on worsted yarn or cloth are made. In the case of cudbear about 3 per cent. will be found a convenient quantity, and about 5 per cent. of orchil. Dye-tests should be made both in neutral and in acid solutions. It is also advisable to dye in the first case neutral, and afterwards add acid (3 per cent. of sulphuric acid) and dye a second lot of material in the same baths. In this manner certain adulterations are easily and readily detected. When *cudbear* is to be examined, the requisite amount is carefully weighed out on the balance and added to the dye-bath, which is kept in ebullition about a quarter of an hour before the material to be dyed is introduced. In the case of *orchil liquor* it is not advisable to weigh out direct, since it would be difficult to obtain a fair average portion in the small amount required for 10 grms. of material. Weigh out 10 grms. of the sample (being careful to shake the bottle immediately before weighing), dilute to 1,000 c.c., and, after well shaking, measure quickly the quantity required in a graduated cylinder. When the temperature of the baths is the same, the yarn or cloth, previously wetted out, is introduced, and dyed for one hour. Whenever samples of orchil liquor are taken from casks, it is most important that the liquid should be thoroughly agitated by means of rakes.

Cudbear and orchil, being somewhat high in price, are frequently adulterated with some of the coal-tar colours, more especially Magenta, and occasionally with some of the red woods. Sometimes both classes of dyes are present. During the past few years many new azo-dyes have been introduced into the market, which yield shades very similar to that of orcein.

Several methods of detecting these various adulterations have been proposed, but many of them are only of any use when the foreign colouring matter is present in comparatively large quantities.

F. Breinl\* has studied the reactions of a number of coal-tar colours similar in shade to orchil. He divides them into three groups—(1) The sulphonic acid derivatives of Magenta, &c. (2) Magenta, and basic colouring matters from Magenta-residue and Safranine. (3) The azo-dyes. The reagents employed for detecting the various adulterations are a mixture of hydrochloric acid and

\* *Mitth. d. Techn. Gewerbemuseums in Wien*, 1887, p. 37; *Journ. Soc. Dyers and Col.*, 1888 p. 46.

stannous chloride, basic lead acetate, common salt, caustic soda, concentrated sulphuric acid, concentrated nitric acid, and concentrated hydrochloric acid.

The most suitable method of proceeding in examining orchil and cudbear is to test them in succession with respect to the single groups. From 1 to 2 grms. of the sample are boiled with 100 c.c. of water and the solution filtered; 15 to 20 c.c. of the tin solution (made by dissolving 10 grms. of stannous chloride in 25 c.c. of concentrated hydrochloric acid and 50 c.c. of water) are added, and again heated to boiling. If, after some minutes of continuous boiling, the liquid appears only yellow or yellowish-brown, no colouring matter of group I. is present; but if the liquid retains a red or reddish-violet colour, Acid magenta, Red-violet, or an acid colouring from magenta-residues is present. With respect to group II. the orchil or cudbear is dissolved in absolute alcohol (about 20 c.c. for 1 gm. of material), and water added until the solution contains about 25 per cent. of alcohol. Basic acetate of lead at 52° Tw. is then added to the solution, in the proportion of about 10 c.c. for every gramme of extract. In this manner the natural colouring matter is precipitated, whilst Magenta, Safranine, &c., remain in solution. If the filtrate is quite or nearly colourless, none of these basic coal-tar colours is present; but if it has a distinct crimson colour and a yellow fluorescence, the sample contains *Safranine*, the presence of which may be confirmed by the sulphuric acid reaction. If, however, the alcoholic filtrate is of a red colour without fluorescence, it is tested, after removal of the alcohol, with nitric acid. If this produces only a yellowish-brown colour without fluorescence, pure *Magenta* is present; but if a yellowish-green fluorescence is perceived, it indicates the presence of a basic colouring matter from magenta-residues (*Corise*, *Grenadine*, &c.).

In order to test for colouring matters of group III. (azo-dyes), a fresh portion of the sample is boiled with water (about 100 c.c. for 1 gm. of substance), left to cool, filtered, and the filtrate saturated with common salt. Most of the coal-tar colours of this group are completely precipitated, but at the same time a little of the orcein is also thrown down. If a precipitate is obtained, it is thrown on a filter and washed with a saturated solution of common salt containing a few drops of dilute caustic soda until the filtrate runs off quite or nearly colourless. If there is still a residue, it is dissolved in hot water and the solution treated, after cooling, with concentrated sulphuric acid. The sulphuric acid is added, so that it may collect at the bottom of the test-tube. If a violet, green, or blue zone is obtained, the presence of a colouring matter of group III. may be stated with certainty; the other reactions, as well as dyeing experiments on wool or silk, will furnish further information as to its nature. If, however, sulphuric acid produces a red or brown zone, this only indicates orcein, which was precipitated by salt and not completely washed out.

A. Kertess\* tests for *Acid magenta* in orchil and cudbear as follows:—A small quantity of the sample is boiled up with water and filtered. The filtrate is mixed in a test-tube with benzaldehyde; equal parts of stannous chloride and hydrochloric acid are added, and the whole well agitated and allowed to settle. If no Acid magenta be present, the lower layer of liquid will appear colourless, while in the presence of that colouring matter it becomes of a magenta colour. The solution should be very dilute for this test.

Liebmann and Studer† propose the following process for the detection of *Magenta* and *Acid magenta* in cudbear and orchil:—1 gm. of the dyestuff is boiled with 100 c.c. of water, and, after cooling, saturated with sulphurous anhydride. Most of the cudbear is thus precipitated. The *Magenta* or sulphonated magenta remains, however, entirely in solution—not as such, but

\* *Journ. Soc. Dyers and Col.*, 1885, p. 217, from *Dingl. Polyt. Journ.*

† *Journ. Soc. Chem. Ind.*, 1888, p. 287.

in combination with sulphurous acid. If now acetone be added to this solution, and Magenta or Acid magenta is present, the colour turns after a few minutes' standing into a violet, while genuine cudbear does not show any change of colour.

The detection and estimation of minute quantities of Magenta in orchil and cudbear have been studied by Rawson.\* The method is based upon the *complete* precipitation of orcein in an aqueous and alcoholic solution by basic acetate of lead, followed by an excess of ammonia. Magenta-base, under the same conditions, remains in solution. It will be observed that the principle is similar to that of Breinl's process, which has been already described; but it had been previously noted that, although basic acetate of lead threw down most of the cudbear, a considerable amount still remained in solution, and it was only after adding an excess of ammonia, or soda, that the natural colouring matter was *completely* precipitated. The process is carried out in the following manner:—

From 1 to 2 grms. of cudbear (or an equivalent amount of orchil liquor) are boiled with 50 c.c. of alcohol, and afterwards diluted with 100 c.c. of water; 15 to 20 c.c. of a strong solution of basic acetate of lead (sp. gr. 1.25) are then added, followed, after stirring, by a similar quantity of strong ammonia. The mixture is filtered, and if the amount of Magenta present is to be *estimated*, the precipitate is washed with a solution containing 1 part of ammonia, 5 parts of alcohol, and 10 parts of water; otherwise the washing may be neglected. With pure cudbear the filtrate is quite colourless; if Magenta be present it is either colourless or pink, according to the amount of ammonia present in the solution. The liquid is then acidulated with acetic acid, when the presence or absence of Magenta is at once made apparent; in the case of pure cudbear or orchil the solution remains colourless, whereas, if a salt of rosaniline be present, the well-known colour of Magenta is immediately developed. If further proof be wanting, a small piece of worsted yarn may be dyed in the solution and afterwards tested in the usual way with such reagents as hydrochloric acid, caustic soda, and a mixture of hydrochloric acid and stannous chloride.

By means of this method 1 part of Magenta in 100,000 parts of cudbear can be detected.

For determining the *amount* of Magenta present a colorimetric process is used. A standard solution of pure Magenta is prepared so as to contain  $\frac{1}{100}$  milligram. per c.c. It is acidulated with acetic acid in order that it may be under the same conditions as the solution to be tested. The latter is made up to a known bulk, say 250 c.c. (or, if the quantity of Magenta present be very small, concentrated to 100 c.c., and the whole taken for estimation), and an aliquot part run into a Nessler tube and diluted to 100 c.c. The standard solution of Magenta is then run from a burette into a second cylinder in such quantity that the depth of colour is equal to that in the first, as in the case of Nesslerising ammonia. The amount of Magenta present in the sample of cudbear or orchil under examination can be then readily calculated. In place of Nessler tubes the colorimeter or Lovibond's tintometer (pp. 813 and 814) might be used with advantage.

The method is also applicable to the detection of Methyl violet and Safranine. The base of the latter is much more soluble in ammonia than the bases of Methyl violet and Magenta. The three colouring matters may be easily distinguished from one another. On the addition of acetic acid to the ammoniacal filtrate, the solution becomes of a bluish-violet tint if Methyl violet be present. Under the same conditions solutions of Safranine and Magenta are pink or bluish-red. Strong ammonia decolourises Methyl violet

\* *Journ. Soc. Dyers and Col.*, 1888, p. 68; *Chemical News*, vol. lvii. (1888), p. 165.



and Magenta, whereas it produces little or no effect upon a solution of Safranine. Strong hydrochloric acid added to a solution of Safranine changes the colour to blue; solutions of Magenta and Methyl violet with the same reagent become of a pale yellow colour. In place of, or in addition to, these tests, a small piece of worsted yarn may be dyed in the neutralised solution (after the removal of the cudbear, as already mentioned), and the colouring matter identified in the usual way on the dyed material.

Azo- or oxyazo-red dyes, when present in cudbear, may usually be readily detected by the formation of a green, blue, or violet-coloured streak when a little of the sample is thrown on the surface of concentrated sulphuric acid. In some cases, however, the colour would scarcely be distinguishable from that given by genuine cudbear, when it would be necessary to make further experiments. For the detection of this class of colouring matters the following mode of procedure gives very satisfactory results:—From 5 to 10 grms. of worsted yarn are dyed (for about an hour) with about 10 per cent. of cudbear either in a neutral bath, or with the addition of a few drops of ammonia. A fresh quantity of yarn is then dyed in the same liquor in exactly the same manner. In this way the greater portion of the cudbear is removed from solution. A small quantity of sulphuric acid (3 per cent. on the weight of the yarn) is now added, and a third lot of worsted yarn dyed in the liquor. The azo-red, under the altered conditions of the bath, works on to the fibre (with a little cudbear), and may be afterwards identified by certain well-known means. At the same time it is advisable, although not absolutely necessary, to treat a sample of cudbear known to be genuine in exactly the same manner.

Samples of cudbear often contain considerable quantities of common salt. This may have been added by the manufacturer merely to reduce the strength of the cudbear to a given standard, or it may have been added as an adulteration. As much as 80 per cent. of common salt has been found in a sample of cudbear. Good genuine cudbear, on incineration, leaves on an average about 6 per cent. of mineral matter, which contains about 1 per cent. of chlorine, as chlorides. For the estimation of mineral matter and chlorides, about 1 grm. of the sample is heated to low redness in a platinum crucible until the residue is of a uniform grey colour. The ash should not be allowed to fuse. If the mineral matter be not more than 7 or 8 per cent., it is quite unnecessary to determine the amount of chlorides. If considerable, the ash is treated with water, and diluted to a known volume, say 500 c.c., and filtered. An aliquot part of the filtrate is then placed in a porcelain basin, a drop or two of potassium chromate added, and titrated with a decinormal solution of silver nitrate.

If orchil liquor be found to contain common salt, it can only be regarded as having been fraudulently added with the intention of raising the specific gravity.

### COCHINEAL.

Genuine samples of cochineal vary very considerably in colouring power. On account of the comparative high price of the dye, it is frequently adulterated, though not at the present day to such an extent as it was formerly.

The value of cochineal samples is best ascertained by making comparative dye-tests. For this purpose several lots of 10 grms. of wool (yarn or cloth) are mordanted with 4 per cent. of stannous chloride and 4 per cent. of tartar. The material should be entered at about 50° C., and the bath gradually raised to the boiling point. After washing, the mordanted wool is dyed in fresh baths, with about 5 per cent. of each sample (ground) for one hour. The tests may also

be made in a single bath (as in cochineal-scarlet dyeing), using in each case 3 per cent. of stannous chloride, 3 per cent. of oxalic acid, and 10 per cent. of cochineal. On comparing the dried swatches, a decision must be made as quickly as possible, otherwise the eye becomes soon fatigued, and is unable to appreciate a small difference in depth of shade. When a number of samples have to be examined the eye should be allowed to rest now and again on cloth dyed a bright green.

Samples of cochineal may also be conveniently estimated by a colorimetric method in the following manner:—0.25 grm. of each sample, finely powdered, is boiled with about 200 c.c. of alcohol for a quarter of an hour, and, on cooling, made up to 250 c.c. with alcohol. 5 c.c. of the filtered solution, with 1 c.c. of a 1 per cent. solution of alum, are introduced into a Nessler tube and diluted with water to 100 c.c. The colour develops gradually in the course of two or three minutes. The samples are compared with a standard, the value being in the inverse ratio of the number of c.c. required to produce the same depth of tint.

Such adulterations as barium sulphate, lead sulphate, &c., may be detected by immersing the cochineal in warm water, when the mineral matters settle to the bottom. The cochineal may also be ignited in a crucible, and the ash examined for adulterations. Genuine cochineal leaves less than 1 per cent. of ash.

### CUTCH AND GAMBIE.

The only reliable method for dyeing purposes is to make comparative dye-tests. The estimation of the amount of catechu-tannic acid present is of no value whatever. Cotton or worsted yarn, in lots of 10 grms. each, is dyed at a boiling temperature with 10 per cent. of cutch and 1 per cent. of copper sulphate for one hour. For wool about a litre of water is used, but for cotton not more than 500 c.c. The dye-liquor is not exhausted, hence it is very important to have exactly the same volume of liquid in each case. The material is allowed to gradually cool in the liquid for a period of three hours, when it is taken out, squeezed, and worked in fresh hot baths for half an hour with 2 per cent. of bichromate of potash. The hanks are then washed, dried, and compared.

Samples of cutch and gambier vary greatly, not only as regards their tinctorial power, but also in respect to the shades which they yield when dyed under identical conditions. Some samples give very red browns, others yellow or olive-browns. Cutch and gambier are frequently adulterated with mineral substances, clay, &c., and occasionally with starch. Excess of mineral matter is readily determined by igniting a weighed amount in a crucible. Good cutch should not leave more than about 3 per cent. of mineral matter. The percentage of water usually varies from 15 to 25, with an average of about 20.

### THE COAL-TAR COLOURS.

With few exceptions, the coal-tar colours as a class (like the natural colouring matters) can only be satisfactorily valued by means of experimental dye-trials. The exact mode of procedure varies according to the properties of the colouring matter and to the purposes to which it is to be applied. General methods of making comparative dye-tests are given on pp. 810-813; and in Part VII. the mode of application of the coal-tar dyes will be found. In conducting these dye-trials a given weight of colouring matter (about 1 grm.), whenever possible, should be dissolved in a litre of water, and an aliquot part taken. With pure colouring matters, as a rule, not more than 0.2 to 0.5 per cent. should be taken. If different classes of blacks are being compared sufficient colouring matter

should also be taken to produce full shades. In the case of paste dyes, such as the Alizarins, from 2 to 5 per cent. will be required. As previously stated under comparative dye-tests, the results are only of value when the conditions in each case are identical, or as nearly so as possible. When comparatively small quantities of colouring matter are used, wool and silk in the majority of cases leave but little colour in the bath. In some cases, however—with Alkali blue, for example—a large proportion of colour is left in the bath. In making comparative tests of such dyes, a second lot of material should always be dyed without any further addition. In many cases colorimetric tests afford much useful information. The observations serve either as a preliminary to making dye-tests, or as a confirmation of them. Colorimetric tests are not of much value unless the dyes under examination are of the same kind, and of a similar shade. Methods of making these tests are given on p. 813, under *Colorimetry*. There are few published methods for determining the value of colouring matters other than by experimental dye-tests.

In the *Journal of the Society of Dyers and Colourists* (1888, p. 82) Rawson describes a "method for determining the value of Naphthol yellow and certain other coal-tar colours." The principle of the process might be applied in numerous other cases.

Naphthol yellow S occurs in the market under various names and of various degrees of strength. Some qualities are practically pure, whilst others contain more or less sulphate or chloride of sodium. The method employed for determining the tinctorial value depends upon Naphthol yellow forming an insoluble precipitate with a solution of Night blue.

A standard solution of *Night blue* is prepared by dissolving 10 grms. in 50 c.c. of glacial acetic acid, and diluting with water to a litre. Solutions of the samples of Naphthol yellow S are prepared so as to contain 1 grm. per litre. The operation is carried out as follows:—10 c.c. of Night blue solution are carefully measured into a small flask, and then about 30 c.c. of the solution of yellow run in from a burette; the mixture is well shaken for about a minute, and then poured on to a filter. If the filtrate be of a distinct yellow colour, a second experiment is performed in a similar manner with a smaller quantity of the solution of yellow; if the filtrate be blue or *even colourless*, more of the yellow solution is required. These experiments are repeated with varying quantities of the Naphthol yellow solution until the filtrate possesses a very faint, scarcely perceptible, yellow tint. It is best to collect the filtrate in clear Nessler glasses. With a little practice, the number of experiments for each sample may be reduced to three or four. The value of the samples under examination will be in inverse proportion to the number of c.c. required to precipitate 10 c.c. of Night blue. For example, if of two samples, one requires 28 c.c. and the other 35 c.c., their relative value will be as 35 : 28, or expressed centesimally as 100 : 80. If it be desired to express the percentage of pure colouring matter present in the samples, the Night blue solution may be standardised by means of recrystallised Naphthol yellow S, which is the potassium salt of dinitro- $\alpha$ -naphthol-sulphonic acid. 1 grm. of *commercial* Night blue precipitates about 0.25 grm. of pure dry Naphthol yellow S. It would thus appear that two molecules of Night blue combine with one molecule of Naphthol yellow S to form the insoluble precipitate.

The method is applicable to the valuation of the azo-dyes, but in such cases it must be used with discretion. Colouring matters which are to be compared with one another must possess a similar constitution. It would not be correct, for example, to compare a Crocein scarlet with a Xylidine scarlet. But a number of samples of either of these scarlets, containing various proportions of either mineral or organic adulterations, can be valued by the Night blue process with great precision.

A. Seyewetz\* has applied the principle of this process to the determination of a number of colouring matters.

P. Kay and J. R. Appleyard,† at the suggestion of Knecht, have applied the process to the valuation of picric acid. In this reaction one molecule of Night blue was found to precipitate one molecule of picric acid. They also found that Crystal violet (hexamethyl-rosaniline hydrochloride) gave a similar insoluble precipitate with picric acid. Kay‡ further shows that picric acid may be estimated by means of a standard solution of caustic potash, using phenolphthalein as an indicator. Of course the method is only applicable in the absence of acid or alkaline salts.

Some coal-tar colours may be estimated by means of a standard solution of sodium hydrosulphite§ in a similar manner to that already described for indigo (p. 820). The operation must be conducted in a closed vessel, from which the air has been expelled by a current of carbon dioxide, and since the decolourisation takes place only at 100° the liquid under examination must be raised to the boiling point. One molecule of dyes, such as Magenta, Hofmann's violet, Paris violet, &c., requires for complete decolouration the same quantity of hydrosulphite as that which is required to reduce two molecules of ammoniacal copper sulphate.

Formaldehyde sulphoxylate (Hyraldite, Rongalite, &c.) with the addition of a little sulphuric acid may be used in certain cases instead of hydrosulphite, when the determination may be made in an open vessel.

Knecht|| has found that many of the azo-dyes, nitro-compounds, basic colours, and Eosins may be estimated by means of titanous chloride. A standard solution of  $TiCl_3$  is prepared as directed under "Analysis of Indigo," p. 822.

The mode of procedure varies somewhat according to the nature of the colouring matter.

**Estimation of Azo-dyes.**—Colouring matters, such as Crystal scarlet, Orange II, Cotton scarlet, &c., which are soluble in dilute hydrochloric acid, may be estimated direct, the dyestuff acting as its own indicator. Solutions are made containing 1 gm. of colouring matter per litre of distilled water. 100 c.c. of such a solution are measured into a conical flask and, after adding 10 c.c. strong hydrochloric acid, boiled for about a minute. The hot solution is then titrated with the standard titanous chloride solution until it is just decolourised. The  $TiCl_3$  solution is of such a strength that 1 c.c. corresponds to about 0.0015 gm. of iron. It is standardised by means of a solution of ferric iron. Colouring matters, such as Orange II, which contain one azo-group require four atoms of hydrogen (equivalent to four of iron) for reduction, and those containing two azo-groups, such as Cotton scarlet, require eight atoms.

*Examples*—1. Orange G ( $C_{16}H_{10}N_2S_2O_7Na_2$ ).—0.5 gm. was dissolved in 500 c.c. water. 100 c.c. with 10 c.c. hydrochloric acid after boiling required 30.1 c.c. titanous chloride.

$$1 \text{ c.c. } TiCl_3 = 0.001277 \text{ gm. Fe.}$$

56 parts of Fe correspond to 113 parts of Orange G ;

$$\therefore \frac{0.001277 \times \frac{113}{56} \times 30.1 \times 100}{0.1} = 77.57 \text{ per cent.}$$

\* *Rev. Gén. des Mat. Col.*, 1901 (5), p. 44; *Journ. Soc. Chem. Ind.*, 1901, p. 394.

† *Journ. Soc. Dyers and Col.*, 1888, p. 84.

‡ *Ibid.*, 1888, p. 84.

§ *Watts' Dict.*, viii., p. 87.

|| *Journ. Soc. Dyers and Col.*, 1903, p. 169; 1904, p. 97; 1905, p. 292.

2. *Cotton Scarlet* ( $C_{22}H_{14}N_4S_2O_7K_2$ ).—0.5 gm. dissolved in 500 c.c. 100 c.c. required 20.4 c.c. titanous chloride.

1 c.c.  $TiCl_3 = 0.001838$  gm. Fe.

56 parts of Fe corresponds to 73.5 parts of Cotton scarlet ;

$$\therefore \frac{0.001838 \times \frac{73.5}{56} \times 20.4 \times 100}{0.1} = 49.20 \text{ per cent.}$$

In the case of dyestuffs which, like the majority of the benzidine derivatives, are thrown out of solution by hydrochloric acid, the reaction is too slow and the end not sufficiently sharp to admit of direct titration. In such cases the acid solution of the colour is treated with an excess of titanous chloride solution and boiled for two minutes, taking the precaution of passing a gentle current of carbon dioxide through the flask during the operation. The flask is cooled and the excess of titanous chloride estimated by a standard solution of iron alum, using potassium sulphocyanide as indicator. By subtracting the number of cubic centimetres of iron alum solution (or their equivalent in titanous chloride, should the two solutions not be of equal strength) from the total number of cubic centimetres of titanous chloride run in, the amount of the latter used in reducing the dyestuff is ascertained.

*Example—Chrysophenine G* ( $C_{30}H_{26}N_4O_8S_2Na_2$ ).—0.5 gm. was dissolved in 500 c.c. 100 c.c. are measured into a conical flask and heated to the boil. 10 c.c. strong hydrochloric acid and 50 c.c. of standard titanous chloride solution were added, and whilst a current of carbon dioxide was passed into the flask the contents were boiled for about two minutes until complete reduction had taken place. After cooling, the excess of  $TiCl_3$  was titrated with iron alum solution (about 14 grms. per litre). 29.7 c.c. were required, and this was equivalent to 30 c.c. of the  $TiCl_3$  solution. Consequently, 20 c.c.  $TiCl_3$  had been used in reducing 0.1 gm. Chrysophenine.

1 c.c.  $TiCl_3 = 0.001742$  gm. Fe.

56 parts Fe correspond to 85 parts of Chrysophenine ;

$$\therefore \frac{0.001742 \times 20 \times \frac{85}{56} \times 100}{0.1} = 52.88 \text{ per cent.}$$

It has been found that certain colours of the Benzidine class (but not yellows) may be estimated by direct titration, using Rochelle salt or sodium bitartrate in place of hydrochloric acid. Benzo-purpurin, Erika, Diamine violet N, and Diamine black have given good results by this method.

*Example—Benzo-purpurin 4 B* ( $C_{33}H_{26}N_6O_8S_2Na$ ).—1 gm. was dissolved in 250 c.c. water. 25 c.c. (= 0.1 gm.) were mixed with 25 c.c. of a 20 per cent. solution of Rochelle salt and boiled. 18 c.c. titanous chloride solution were required.

1 c.c.  $TiCl_3 = 0.001742$  Fe.

56 parts Fe correspond to 90.5 parts of Benzo-purpurin 4 B ;

$$\therefore \frac{0.001742 \times \frac{90.5}{56} \times 18 \times 100}{0.1} = 50.67 \text{ per cent.}$$

**Estimation of Nitro-compounds.**—As with the azo-dyes, the reduction of nitro-compounds takes place quantitatively, the nitro-groups being reduced to the corresponding amido-groups. Each nitro-group requires six atoms of hydrogen for its complete reduction. For the estimation of nitro-compounds the indirect method, as described for Chrysophenine, must be employed.

Boiling with excess of titanous chloride should be continued for about five minutes.

*Example—Naphthol Yellow S* ( $C_{19}H_4N_2O_6SNa_2$ ).—0.5 gram. dissolved in 500 c.c. water. 25 c.c. boiled with 10 c.c. hydrochloric acid and 50 c.c. titanous chloride afterwards required 27.6 c.c. iron alum solution of same strength as  $TiCl_3$ . Therefore, 22.4 c.c.  $TiCl_3$  were used.

$$1 \text{ c.c. } TiCl_3 = 0.001792 \text{ gram. Fe.}$$

672 parts of Fe correspond to 358 parts of Naphthol yellow S ;

$$\therefore \frac{0.001792 \times \frac{358}{672} \times 22.4 \times 100}{0.025} = 85.53 \text{ per cent.}$$

Picric acid ( $C_6H_3N_3O_7$ ) is estimated in a similar manner.

1,008 parts of Fe correspond to 229 parts of picric acid.

**Estimation of Basic Colours.**—The general method consists of adding 25 c.c. of a 20 per cent. solution of Rochelle salt to 50 c.c. of the colour solution, boiling and titrating with titanous chloride in a current of carbon dioxide as described for Benzo-purpurin 4 B. Magenta, Acid magenta, Crystal violet, Malachite green, and Indoine have been examined by this method.

*Example—Magenta* ( $C_{19}H_{18}N_3Cl$ ).—1 gram. was dissolved in 500 c.c. water. 50 c.c. with the addition of 25 c.c. of a 20 per cent. Rochelle salt solution were heated to the boil and titrated with titanous chloride. 14.2 c.c. were required.

$$1 \text{ c.c. } TiCl_3 = 0.001622 \text{ gram. Fe.}$$

323.5 parts of Magenta correspond to 112 parts of iron.

$$\therefore \frac{0.001622 \times \frac{323.5}{112} \times 14.2 \times 100}{0.1} = 66.53 \text{ per cent.}$$

Methylene blue is best titrated alone or with the addition of hydrochloric acid in place of Rochelle salt.

319.5 parts of Methylene blue ( $C_{16}H_{18}N_3SCl$ ) correspond to 112 parts of iron.

**Estimation of Eosins and Rhodamines.**—These colouring matters are not easily reduced, especially in acid solution. By heating a solution of Eosin or Rhodamine in presence of Rochelle salt with  $TiCl_3$ , decolourisation ensues after a time, but the solution becomes turbid owing probably to the separation of the leuco-compound, and the end reaction is in consequence not clear. But by the addition of alcohol to the mixture a perfectly sharp and distinct end reaction is obtained.

*Example—Rhodamine B* ( $C_{28}H_{31}N_2O_4Cl$ ).—1 gram. was dissolved in 500 c.c. water. 50 c.c. mixed with 25 c.c. 20 per cent. Rochelle salt solution and 50 c.c. of alcohol were boiled and titrated. 10.6 c.c.  $TiCl_3$  were required. 25 c.c. Rochelle salt and 50 c.c. alcohol alone used 0.3 c.c.  $TiCl_3$ .

$$1 \text{ c.c. } TiCl_3 = 0.001901 \text{ Fe.}$$

478.5 parts of Rhodamine B correspond to 112 parts of iron ;

$$\therefore \frac{0.001901 \times \frac{478.5}{112} \times 10.3 \times 100}{0.1} = 83.65 \text{ per cent.}$$

Whatever means are adopted to determine the *amount* of colouring matter present in commercial dyes, practical dye-tests will always be required to ascertain the shades which they are capable of producing on the textile fibres.

*Impurities.*—Some of the commercial artificial dyes consist of practically pure colouring matters, many others contain more or less impurities of manufacture, and a numerous class contain mineral salts as well as organic substances purposely added. Sodium chloride, sodium sulphate, and dextrin are the most common substances present, but sodium carbonate, magnesium, potassium, and ammonium salts may occasionally be found. The presence of any of these bodies in an artificial dye does not generally indicate adulteration, unless, of course, the product is represented as a *pure* colouring matter. In most cases the pure colouring matter cannot be conveniently prepared on a commercial scale, and as the manufactured product is liable to vary in strength, it is reduced to a given standard by some inert substance. Sodium sulphate is used largely for azo-dyes; dextrin and common salt for basic dyes.

*Sulphates* may usually be detected by adding hydrochloric acid and barium chloride to a dilute solution of the dye. In some cases it is preferable to precipitate the colouring matter by *pure* sodium chloride, and test the filtrate as above. Alkaline salts of sulphonated dyes leave, on ignition, alkaline sulphates, so that the presence of a sulphate in the ash does not indicate the presence of sodium sulphate in the colouring matter. In the absence of sulphates, the detection of sulphuric acid in the ash indicates the presence of a sulphonic acid group or groups in the colour.

*Chlorides* in many cases may be detected by simply adding nitric acid and silver nitrate to a dilute solution of the dye. If the colouring matter is soluble in strong alcohol, it should be extracted by warming with that solvent and the residue tested for common salt.

*Dextrin* may generally be recognised by its smell when the dye is dissolved in warm water; also by its insolubility in alcohol. When it has been mixed in the dry state (which is usually the case), it is best detected by means of the microscope.

*Mixed Dyes.*—Many of the dyes found in commerce sold under various names are mixtures of two or more colouring matters. When the dyes have been mixed in the powdered state, they may be recognised in the following manner:—A filter paper is moistened with water or alcohol, and a little of the powdered dye is gently blown on to it. Each particle slowly dissolves, forming a little streak, and if more than one colouring matter is present it is readily detected. Mixtures of many of the azo-dyes are more easily recognised by blowing a little of the powdered substance over the surface of concentrated sulphuric acid contained in a porcelain basin. When the colouring matters have been mixed in solution and evaporated together, the above tests are not reliable. In such cases successive lots of wool, silk, or cotton are dyed in a solution of the sample and the shade compared. The dyed swatches are dried, and small pieces tested with various reagents. If the sample was a mixture, the first swatch dyed will probably show different reactions to the last. Mixtures of dyes may also be detected by means of *capillary analysis*.

The following abstract of a paper by Goppelsröder on this subject is taken from the *Journal of the Society of Dyers and Colourists*, 1888, p. 5:—\*

Based upon some experimental researches of Schönbein in 1862, which showed that different substances when dissolved in water have a different velocity of propagation by capillary attraction in porous material, such as unsized paper, Goppelsröder has examined in particular the behaviour of colouring matters in this respect. The colouring matters, or mixtures of them, were, if possible, dissolved in water or alcohol, or, if the liquids proved ineffective, in some other solvent which had no chemical action. The porous

\* For a fuller account see *Capillary Analysis*. By F. Goppelsröder, Basel. Emil Birkhäuser, 1901. See also D. Paterson, *Journ. Soc. Dyers and Col.*, 1893, p. 110.

medium employed was pure (Swedish) white filtering paper, cut into strips of different breadth and length, according to the quality and complexity of the (not concentrated) colour solution under examination. A number of such strips of paper were suspended at one end, while 5 to 10 millimetres of the other ends were made to dip into the solution contained in a series of glasses. The time of immersion was usually fifteen minutes. By the action of capillary attraction the water contained in the solution begins to rise in the paper, reaching a greater height in a given time than all other substances. Picric acid stands next in velocity of rising, and by dipping a strip of filtering paper into an aqueous solution containing picric acid and turmeric, three different zones will appear on it after a given time—a highest narrow zone containing water, a middle broad zone of yellow picric acid, and a third and lowest zone of the appearance of the yellow colouring matter of turmeric. By immersing the strip of paper into a dilute solution of potash, the zone of picric acid disappears, while the zone with the turmeric turns brown; a single operation is, therefore, sufficient for nearly complete separation of the two colouring matters. If now the lowest zone of turmeric yellow is cut off, and the colouring matter contained in it dissolved in alcohol, a repetition of the operation with a fresh strip of paper will again produce three zones—the highest containing alcohol, the middle zone a few lines in breadth, and coloured a very faint yellow with the picric acid. The turmeric zone turns brown in gaseous ammonia, while the zone of picric acid remains unaltered; in a weak alkaline solution the latter is decolourised, the picric acid being dissolved.

By operating upon a mixture of an aqueous solution of picric acid and one of indigo extract, four zones were obtained, when the solution had a purely green colour without prevalence of blue or yellow—a lowest broad zone of a greenish colour, above it a second much narrower zone of pure yellow, above this a third zone containing dilute sulphuric acid, and a fourth zone containing pure water, a drop of tincture of litmus not turning red when applied to it. Three zones only were obtained from a mixture of a little picric acid with much indigo extract—a lowest rather broad zone of an intense bluish-green, a middle purely yellow zone, and a highest zone of sulphuric acid, no water being separated in this case.

In commercial Magenta prepared by the reaction of arsenic acid on aniline-oil, traces, at least, of a yellow colouring matter could always be distinctly detected by capillary analysis. But if the filtering paper is dipped a few millimetres into an alcoholic solution of a well crystallised salt of rosaniline, four zones are observed after a few minutes; a highest colourless zone of pure alcohol, and three others of a light pink, pink and deep red in succession. An addition of a trace only of picric acid produces (1) a pink and deep red coloured zone, (2) a colourless zone, (3) a narrow zone of picric yellow. The more picric acid was added to the Magenta, the broader was the yellow zone of picric acid, and the narrower the brownish-red zone of Magenta. Samples of commercial Magenta produced, besides the red zone, a more or less broad yellow zone, which appears most distinct if the alcoholic solutions of Magenta are employed in a very concentrated state, and if the filter paper is immersed long enough for the deposition on it of the Magenta with a dark brownish-red colour.

**Identification of Artificial Colouring Matters.**—Much information may usually be obtained regarding an unknown colouring matter by dyeing cotton, wool, and silk under various conditions. For this purpose a small water bath, with six apertures to receive little beakers or boiling tubes, may be used with advantage. A solution of the colouring matter is placed in each vessel, and the following tests made:—



- No. 1. Unmordanted wool ; solution neutral.  
 „ 2. „ „ „ with addition of a few drops of dilute sulphuric acid.  
 „ 3. Wool mordanted with bichromate of potash ; solution neutral.  
 „ 4. Unmordanted cotton ; solution neutral.  
 „ 5. „ „ „ with addition of a little sodium sulphide.  
 „ 6. Cotton mordanted with tannic acid and tartar emetic ; solution neutral.

The above tests may, of course, be varied or supplemented as desired. After boiling for about a quarter of an hour, the small swatches are taken out and washed, when the results will broadly indicate the class of colouring matter to which the dye belongs. The dyed material may then be dried and tested with various reagents.

Witt,\* in 1886, proposed the first definite scheme for the identification of coal-tar dyes, separating them into groups according to their colour, solubility, and behaviour with caustic soda.

Weingärtner,† in 1887, published a much more extended scheme, classifying the dyes into “acid” or “basic,” according to their reaction with tannic acid ; and into smaller groups by their behaviour upon reduction with zinc dust.

Taking Weingärtner's scheme as a basis, A. G. Green‡ has worked out a much more satisfactory process, by means of which a very large number of dyes may be identified. The main reactions made use of are :—

1. Solubility or insolubility in water.
2. Precipitation or non-precipitation by tannic acid.
3. Reduction by zinc dust with subsequent re-oxidation.

Whilst the derivatives of triphenylmethane after reduction are re-oxidised by air only with great difficulty, the azines, oxazines, thiazines, and acridine colours all re-appear with great rapidity on exposure of the reduced solutions to the atmosphere. Green makes use of this difference of behaviour, which is very marked, to differentiate these two groups of colours. On the other hand, the triphenylmethane colours are distinguished from those which do not yield leuco-compounds, but are completely broken up on reduction by the colour of the reduced solution being restored by chromic acid. The Quinoline and Primuline colours are distinguished from other dyestuffs by the great difficulty with which they are reduced—Primuline, for instance, remaining unaltered after long boiling with zinc dust and ammonia.

The analytical scheme which is based upon these reactions is contained in the annexed tables.

The tables do not contain all the more recent dyestuffs, especially not the new vat colours and the sulphide colours. These two classes of colouring matters are either insoluble or very sparingly soluble in water or in caustic soda-lye, but readily dissolve on reduction with sodium hydrosulphite. The sulphide colours readily dissolve in a solution of sodium sulphide, and in such solution cotton is dyed direct (see also p. 448 and p. 659, *et seq.*).

\* *Chem. Ind.*, vol. ix., p. 1. Abstracted in *Journ. Soc. Chem. Ind.*, 1886, p. 249.

† *Chem. Zeit.*, 1887, p. 135. Abstracted in *Journ. Soc. Dyers and Col.*, 1887, p. 66.

‡ *Journ. Soc. Chem. Ind.*, 1893, p. 3.

ANALYTICAL SCHEME.

- Group Reagents.—  
 { 1. A solution containing 10 per cent. of tannin and 10 per cent. of sodium acetate.  
 2. Zinc dust and dilute hydrochloric acid, or zinc dust and aqueous ammonia.  
 3. Solution containing 1 per cent. of chromic acid (for basic colours).  
 4. Solution containing 1 per cent. of chromic acid or potassium bichromate and 5 per cent. of sulphuric acid (for acid colours).  
 Distinguishing Reagents.—The members of the same group are distinguished from each other by their reactions with the various reagents and alkalis, concentrated sulphuric acid, alcohol, &c., and by their dyeing properties. See the reactions of the various colours as given by Witt, Weingartner, and others.

GROUP I.—DYE-STUFFS SOLUBLE IN WATER.

A.—Precipitated by Tannin Solution: Basic Colours.

The aqueous solution is reduced with zinc dust and hydrochloric acid and a drop of the decolorised solution put on filter paper. If the colour does not quickly return on exposure to air, the spot is touched with a drop of 1 per cent. chromic acid solution.

Red.	Orange and Yellow.	Green.	Blue.	Violet.	Red.	Green.	Blue.	Violet.	The colour re-appears very slowly or not at all on exposure to air; but returns on spotting with 1 per cent. chromic acid solution: Triphenylmethane Colours, and Basic Phthalates.	The original colour does not return at all.
Tolylene Red. Safranin.	Phosphine. Benzotriazine.	Azine Green.	Methylene Blue. New Methylene Blue N.	Mauve. Amethyst.	Magenta. Isorubine.	Malachite Green. Brilliant Green.	Victoria Blue B.* Victoria Blue ‡ R.	Methyl Violet. Crystal Violet.		Auramine. † Thioharine T. ‡
Pyronine. Acridine Red.	Acridine Yellow. Acridine Orange.		Thionine Blue. Toluidine Blue. Meldok's Blue. Muscarine. Neutral Blue. Basic Blue R and B E. New Methylene Blue G G. Nile Blue. Capri Blue. Fast Black. Induline M. Metaphenyleno Blue B. Paraphenyleno Blue. Indulines.	Neutral Violet. Fast Neutral Violet. Prune. Paraphenyleno Violet. Indulines.	†Rhodamine.	Methyl Green. Iodine Green.	Night Blue.	Hofmann Violets. Benzyl Violet. Ethyl Purple. Regina Purple		Chrysoidine. Blamark Brown. Tannin Orange. New Phosphine. Asc-phosphina. Indoline. † Naphthidine. † Janus Colours. †

The original colour quickly re-appears on exposure to air: Azine, Oxazine, Thiazine, and Acridine Colours.

The colour re-appears very slowly or not at all on exposure to air; but returns on spotting with 1 per cent. chromic acid solution: Triphenylmethane Colours, and Basic Phthalates.

\* The shade which returns is much greener than the original.  
 † The reduced solution gives a beautiful violet when the spot on filter paper is warmed over a flame till dry.  
 ‡ It is only reduced with difficulty and very slowly. † The colour returns more quickly than with the resubline. ‡ It is only reduced with difficulty and very slowly.

ANALYTICAL SCHEME—Continued.  
B.—Not Precipitated by Tannin Solution: Acid Colours.

The aqueous solution is reduced with zinc dust and hydrochloric acid, or with zinc dust and ammonia, and a drop of the decolourised solution is put on filter paper. If the colour does not quickly return on exposure to air, the spot is touched with a drop of chromic acid solution (1 per cent. CrO<sub>3</sub> + 5 per cent. H<sub>2</sub>SO<sub>4</sub>), warmed over a flame, and then held in the vapour of ammonia.

The solution is decolourised.		Not decolourised (by zinc and ammonia), but changed to normal colour. Original colour returns quickly on exposure to air.	Very slowly and incompletely decolourised (zinc and ammonia).	Not altered by zinc and ammonia; very slowly or not at all by zinc and hydrochloric acid.
<p>The original colour does not re-appear on exposure to air, or only very slowly, but returns with chromic acid, and exposure to ammonia vapour.</p>	<p>The ether remains colourless:</p> <p><i>Sulphonated triphenylmethane colours</i>— Acid Magenta. Acid Violet. Formyl Violet. Alkali Blues. Soluble Blues. Patent Blue. Fast Green, bluish. Acid Greens. Guinea Green. Chrome Violet.</p>	<p>Alizarin S. Alizarin Blue S. Cerulein S.</p>	<p>Clayton Yellow. Thiazol Yellow. Turme. Inc. Mimosa.</p>	<p>Quinoline Yellow S. Primuline. Thiofastine S. Oxyphenine. Diamine Fast Yellow B, FF. Chloramine Yellow.</p>
<p>The ether extracts the colour-acid, leaving the aqueous solution nearly colourless:</p> <p><i>Phthalenes and Aurines</i>— Uranine. Chrysoline. Eosin. Erythrin. Phloxin. Erythrosin.* Rose Bengal.* Cyclamin.* Aurine. Coraline.</p>	<p>Defragrates with production of coloured vapours:</p> <p><i>Nitro colours</i>— Picric Acid. Marsin Yellow. Naphthol Yellow S. Auroline.</p>	<p>Burns quietly or defragrates slightly, giving off coloured vapours:—<i>Azo, nitro, and hydrazine colours.</i></p>	<p>Burns quietly or defragrates slightly, giving off coloured vapours:—<i>Azo, nitro, and hydrazine colours.</i></p>	<p>Is stripped by warm soap.</p>
<p><i>Sulphonated azines, coarazines, thiazines, &amp;c.</i>— Soluble Indulines.† Soluble Nigrosines.† Resorcin Blue. Aurine. Thiocarmine. Beale Blue B.S. and B.B.S. Gallamine Blue. Galloycauline. Gallanic Indigo P.S. Indigo-carmine. Saffrosine. Azo-carmine. Mikado Orange.† Rosinduline. Diamine. Fast Yellow A.</p>	<p>Resists warm soap.</p>	<p>Substantive Azo-colours.</p>	<p>Ordinary Azo-colours. Naphthol Green B. Tartrazin. Flavazin. Pyrazine Yellow.</p>	<p>† If the reduction is carried too far, the colour does not return.</p>

\* Iodine is separated by the chromic acid, but disappears on exposure to ammonia.

## ANALYTICAL SCHEME—Continued.

## GROUP II.—DYESTUFFS INSOLUBLE IN WATER.

The powder or paste is treated with water and a few drops of 5 per cent. caustic soda solution.

The colour dissolves.		The colour remains insoluble.		Insoluble in 70 per cent. alcohol.  Indigo.  (Aniline Black).
Soluble in 70 per cent. alcohol.		Solution not fluorescent.		
The alkaline solution is heated with zinc dust and ammonia, and a drop is put on filter paper.		Solution fluorescent.	Solution fluorescent.	
Decolourised or changed to light brown. The original colour returns very quickly on exposure to air.	Decolourised or changed to brown. The original colour does not re-appear on exposure to air.	On adding caustic soda (33 per cent.) to the alcoholic solution.	On adding caustic soda (33 per cent.) to the alcoholic solution.	
Cerulein.	Allizarin.	Colour becomes reddish-brown.	Fluorescence destroyed.	
Gallein.	Anthrapurpurin.		Magdala Red.	Spirit Eosina. Cyanosin.
Gallocyanine.	Flavopurpurin.			
Gallianilic Violet B.S.	Allizarin Orange.	Colour not altered.		
Gallianilic Blue F.	Allizarin Brown.		Endophenol.	
Galloflavin.	Allizarin Bordeaux	Induline (spirit soluble).		
Allizarin Blue.	Patent Fustic.	Nigrosine (spirit soluble).		
Allizarin Black.	Myrtle or Russian Green.	Rosaniline Blue (spirit soluble).		
Allizarin Cyanine.	Gambin B and Y.	Diphenylamine Blue (spirit soluble).		
Allizarin Cyanine Black	Dioxin			
Rauhallol.				
Allizarin Green G & B.				

The reduction with zinc dust requires to be performed with some care. It is usually best to add a little zinc dust to the hot solution of the colouring matter contained in a test tube, agitate, and then add dilute hydrochloric acid drop by drop until decolourised. An excess of acid must be carefully avoided. In other cases, more especially when the colour acid is very insoluble, the reduction must be performed with zinc dust and ammonia; but it is usually safest to repeat the tests with both methods of reduction.

Whilst it is important that the colouring matter should be completely reduced, care should also be taken that the reduction is not carried too far, for some colouring matters (*e.g.*, Indulines) which usually form oxidisable leuco-compounds are thereby completely altered. When reduced the solution is poured off from the greater part of the zinc dust on to a piece of white filter paper and exposed to the air; filtration is unnecessary, as a little zinc 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 a 1 per cent. solution of chromic acid (with addition of sulphuric acid for acid colours). Warming gently for a few seconds over a flame facilitates the reactions, and should also be employed when the reduction has been performed with zinc dust and ammonia, in order to remove the excess of the latter before adding chromic acid, which would otherwise be neutralised.

In the case of acid colouring matters, the paper, after spotting with chromic acid, should be held over a bottle of strong ammonia, for some acid colours (*e.g.*, the Eosins) do not show their true colour whilst acid. On reduction of those Eosins which contain iodine, a brown spot of the latter is obtained with chromic acid, but this disappears on exposure to ammonia vapour, and the original colour of Eosin (or a rather yellower shade) returns. As already pointed out by Weingärtner, great care must be taken that one is not led astray by secondary colours formed by oxidation of the diamines and amidophenols obtained by reduction of azo-colours.

A. G. Rota\* has devised a method for the recognition of coal-tar dyes, chiefly based on their behaviour on reduction in very dilute solution (1 in 10,000). The aqueous or alcoholic solution is diluted to about 1 : 10,000, and 5 c.c. of this are treated with 4 to 5 drops of concentrated hydrochloric acid and the same quantity of a 10 per cent. stannous chloride solution obtained by dissolving tin in hydrochloric acid. The mixture is shaken, and, if necessary, heated to boiling. If the solution does not decolourise entirely, the dyestuff is to be still further diluted or a further quantity of stannous chloride added. Accepting Armstrong and Nietzki's quinone theory, it would appear that under certain conditions stannous chloride reduces those dyestuffs which can be referred to the mono- and di-imido types, whilst those in which one oxygen atom is replaced by a divalent carbon group are not reduced. Thus considering O : R : O as an *o*- or *p*-quinone, dyestuffs belonging to the nitro, nitroso, azo, and quinone imide groups—*i.e.*, having the constitution O : R : N (oxyquinone-imide), or . N : R : N (quinonedi-imide)—are reducible, whilst oxyquinone and triphenylmethane dyestuffs O : R : C (oxycarboquinone) and . N : R : C (imido-carboquinone) are not reduced. The reduced solution after neutralisation with potash lye is treated with a few drops of ferric chloride, or is shaken with air. Some solutions remain unchanged, whilst in others the dyestuff is regenerated. Belonging to the former are the nitro, nitroso, and azo dyestuffs which give stable amines on reduction, whereas the latter, the quinone imido derivatives, forming leuco derivatives, are easily oxidised. The non-reducible dyestuffs can be further divided into two classes, the oxycarboquinone and the imidocarboquinone derivatives. The latter include the Magentas, Acridines, &c., which on treatment in hot aqueous solution with caustic potash lye are decolourised

\* *Chem. Zeit.*, 1898, p. 437; *Journ. Soc. Chem. Ind.*, 1898, p. 798.

or precipitated, whilst the former, by virtue of their acid character, give coloured salts with alkalis usually easily soluble in water. Dyestuffs can thus be divided into four groups, to which two or three large subdivisions belong having similar chromophores, the difference depending upon the different salt forming groups amido, imido, carboxyl, or sulphonic acid. The detection of these is effected by means of suitable fibres, as will be shown later. The dyestuff is examined by the help of the following tables :—

TABLE A.

## CLASSIFICATION OF ORGANIC DYE STUFFS.

A portion of the aqueous or aqueous alcoholic solution of the dyestuff is treated with hydrochloric acid and then with stannous chloride solution.

The solution is decolourised.* Reducible dyestuffs. The decolourised solution after neutralisation with potash lye or sodium acetate is oxidised with ferric chloride or atmospheric oxygen.	
No change. Non-oxidisable dyestuffs.  Group I. Nitroso, nitro, and azo dyestuffs including azoxy and hydrazo colours	Original colour returns Re-oxidisable dyestuffs.  Group II Indogenide and quinone imide dyestuffs.
No further change than with hydrochloric acid alone Non-reducible dyestuffs. A portion of the original solution is treated with 20 per cent. potash lye, and warmed if necessary.	
Solution decolourised or a precipitate is formed. Imidocarboquinone dyestuffs.  Group III. Amido derivatives of di- and triphenyl methane, Auramines, Acridines, Quinolines, and thio-benzenyl dyestuffs.	No precipitate, the colour becomes more intense. Oxycarboquinone dyestuffs  Group IV. Non-amidated diphenyl methane dyestuffs, oxo-ketone dyestuffs (including most of the natural organic dyestuffs).

\* Some Indulines are only decolourised with difficulty, the solution never becoming quite colourless.

TABLE B.

## GROUP I.—DYESTUFFS REDUCIBLE WITH STANNOUS CHLORIDE AND HYDROCHLORIC ACID, THE COLOUR NOT RETURNING ON OXIDATION.

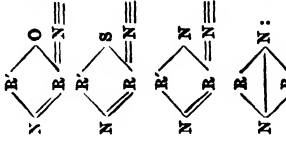
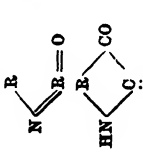
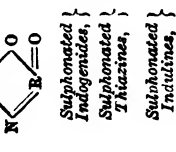
<p><b>Nitro Dyestuffs.</b> E. NO<sub>2</sub>.—Yellow or orange dyestuffs, soluble in water; dyeing wool and silk directly, but not cotton. The aqueous solution tends to decolorise with hydrochloric acid. On partial reduction with hydrochloric acid and stannous chloride, they give red nitro-amido derivatives (nitro-amines) or nitrophenols turning red in potash lye.</p>	<p>Nitro-amines soluble in ether in presence of KOH. . . . . N : R : N</p> <p><i>Unsulphonated</i>, soluble in ether, in presence of acetic acid, . . . . . O : R : N</p> <p><i>Nitrophenols</i> insoluble in ether in presence of KOH, . . . . . H</p>	<p>e.g., Aurantia.</p> <p>e.g., Victoria Yellow.</p> <p>Naphthol Yellow S.</p>
<p><b>Nitroso Dyestuffs.</b> O : B : N : OEL.—Brown or green, usually insoluble in water. Dye indirectly, give a blue coloration with sulphuric acid and puenol (Liebermann's reaction).</p>	<p><i>Unsulphonated</i>, insoluble in alcohol, soluble in ether in presence of acetic acid, . . . . .</p> <p><i>Sulphonated</i>, soluble in water, insoluble in ether, . . . . .</p> <p>The solution is coloured, the colour being extracted by dilute acetic acid, . . . . .</p> <p><i>Basic dyestuffs</i>, . . . . .</p> <p>Coloured solution. The colour is not extracted by dilute acetic acid, . . . . .</p> <p><i>Neutral dyestuffs</i>, . . . . .</p>	<p>. N : B : N . NHR, e.g., Bismarck Brown.</p> <p>O : B : N . NHR, e.g., Sudan I.</p>
<p><b>Azo Dyestuffs.</b> E. N : N : R.—Recognisable as not belonging to either of the two foregoing subdivisions. Their aqueous solutions treated with potash lye and extracted with ether behave as follows:—</p>	<p><i>Unsulphonated</i>, soluble in ether from dilute acetic acid, . . . . .</p> <p><i>Sulphonated</i>, insoluble in ether from dilute acetic acid, . . . . .</p> <p>Colourless solution; acetic acid does not extract anything</p> <p><i>Acid dyestuffs</i>, . . . . .</p>	<p>Dye cotton indirectly } Diamond Yellow.</p> <p>Dye cotton directly } Chrysaline.</p> <p>Dye cotton directly } Bordeaux B.</p> <p>Dye cotton directly } Azo Blue.</p> <p>Dye cotton indirectly } East Yellow N.</p> <p>Dye cotton directly } Congo Red.</p>

\* Some amido-azo dyestuffs (Aniline Yellow) behave like neutral dyestuffs, but differ from these in being decolorised by nitrous acid.

† The presence of an amido group is detected by treating 5 c.c. of the warm solution with two to three drops of 1 per cent. dilute acetic acid and the same quantity of a 1 per cent. potassium nitrite solution. Amido derivatives are decolorised or the colour is modified, whilst non-amidated compounds remain unchanged or are not further affected than by acetic acid alone.

T A B L E C.

GROUP II.—DYE STUFFS REDUCIBLE WITH STANNOUS CHLORIDE AND HYDROCHLORIC ACID, THE COLOUR RETURNING ON OXIDATION.

<p>The solution is coloured parts the original colour to 5 per cent. acetic acid when shaken with it.</p> <p><i>Basic Dye-stuffs.</i>—Dye wool from an alkaline bath.</p>	<p>The solution is easily reduced by hydrochloric acid and stannous chloride in the acid.</p> <p>The solution is only reduced with difficulty and frequently imperfectly. It requires to be warmed, and an excess of hydrochloric acid and stannous chloride.</p>	<p><i>Oxazines</i> (free from sulphur).</p> <p><i>Thiazines</i> (contain sulphur).</p> <p><i>Indulines.</i>—Blue colour with concentrated sulphuric acid, giving a blue solution on dilution with water.</p> <p><i>Safranines.</i>—Green colour with sulphuric acid, turning blue and then violet on dilution.</p>		<p>e.g., Meldola's Blue.</p> <p>e.g., Methylene Blue.</p> <p>e.g., Spirit-soluble Induline.</p> <p>e.g., Safranin I extra.</p>
<p><i>Coloured.</i>—The colour is not extracted by acetic acid.</p> <p><i>Neutral Dye-stuffs.</i>—Insoluble in water; soluble in alcohol; dye the fibre from an indigo vat.</p>	<p>Blue dye-stuffs affected by warm hydrochloric acid.</p> <p>Red or blue dye-stuffs unchanged by hydrochloric acid; give isatine with nitric acid.</p>	<p><i>Indaphenols.</i></p> <p><i>Indogonides.</i></p>		<p>e.g., Indophenol.</p> <p>e.g., Indigotin.</p>
<p><i>Colourless.</i> acetic acid does not extract anything.</p> <p><i>Acid Dye-stuffs.</i>—Soluble in water; dyeing wool from an acid bath.</p>	<p><i>Unsulphonated.</i>—Soluble in ether in presence of acetic acid.</p> <p><i>Sulphonated.</i>—Not soluble in ether.</p>	<p><i>Oxazonet.</i></p> <p>Easily reduced by stannous chloride and hydrochloric acid.</p> <p>Reduced with difficulty by stannous chloride and hydrochloric acid.</p>		<p>e.g., Fluorescent Blue, Orcein.</p> <p>e.g., Indigo-carmine.</p> <p>e.g., Thio-carminine R.</p> <p>e.g., Water-soluble Nigrosines.</p>

\* The Indulines and Safranines differ in their basicity; the former can be liberated by ammonia and extracted by ether, whilst potash is necessary to obtain Safranin base.



**T A B L E D.**  
**GROUP III.—DYE-STUFFS NOT REDUCED BY STANNOUS CHLORIDE AND HYDROCHLORIC ACID HAVING THE IMIDO QUINONE CARBON CHROMOPHORE N : R : C.**

<p>The colour is not extracted by acetic acid from the coloured ethereal dye-stuffs. Neutral dye-stuffs. Insoluble in water; soluble in alcohol.</p>	<p>The ethereal solution is colourless, and does not fluoresce. The solution in acetic acid is pink and fluorescent. The aqueous solution is decolourised by potash.</p>	<p>Colourless, non-fluorescent, ethereal solution. The solution in acetic acid is non-fluorescent. The aqueous solution is decolourised by potash, and decomposed by hydrochloric acid.</p>	<p>Auramines, . . . . .</p>	$\begin{array}{c} R \\   \\ C \equiv N - \\   \\ R \end{array}$	<p>e.g., Auramine O.</p>
<p>The colour is not extracted by acetic acid from the coloured ethereal dye-stuffs. Insoluble in water; soluble in alcohol.</p>	<p>Colourless, greenish, fluorescent, ethereal solution. The aqueous solution is precipitated by potash, and only slightly changed by hydrochloric acid. Nitric acid colours it red.</p>	<p>Colourless, greenish, fluorescent, ethereal solution. The acetic acid extract is reddish-violet, blue, and green, without fluorescence. The aqueous solution is generally decolourised by potash on warming, and is turned yellow by hydrochloric acid (with the exception of the phenylated rosanilines).</p>	<p>Acridines, . . . . .</p>	$\begin{array}{c} R & & N \\ & \diagdown & / \\ & C & \\ & / & \diagdown \\ R & & R \end{array}$	<p>e.g., Phosphine.</p>
<p>The colour is not extracted by acetic acid from the coloured ethereal dye-stuffs. Insoluble in water; soluble in alcohol.</p>	<p>The ethereal solution is colourless, and does not fluoresce. The solution in acetic acid is pink and fluorescent. The aqueous solution is decolourised by potash.</p>	<p>Rosanilines (unaulphoned). . . . .</p>	<p>Rosaminines (unaulphoned). . . . .</p>	$\begin{array}{c} R \\   \\ C - R \\   \\ R = N - \end{array}$	<p>e.g., Magenta.</p>
<p>The colour is not extracted by acetic acid from the coloured ethereal dye-stuffs. Insoluble in water; soluble in alcohol.</p>	<p>The ethereal solution is yellow, and does not fluoresce. The alcoholic solution is yellow and non-fluorescent, and is unaltered by aqueous acids or alkalis.</p>	<p>Pyronines (are turned yellow by hydrochloric acid). Rhodamines (unaulphoned, are unaffected by hydrochloric acid).</p>	<p>Quinophthalones* (unaulphoned).</p>	$\begin{array}{c} R & & O \\ & \diagdown & / \\ & C & \\ & / & \diagdown \\ R & & R \end{array}$	<p>Pyronine G. e.g., Rhodamine S.</p>
<p>The ethereal solution is colourless, and does not fluoresce. The alcoholic solution is yellow and non-fluorescent, and is unaltered by aqueous acids or alkalis.</p>	<p>Yellow dyestuffs soluble in water without fluorescence; unchanged by aqueous acids or alkalis.</p>	<p>Sulphonated Quinophthalones, } Sulphonated Rosanilines, } Sulphonated Rhodamines, }</p>	<p>Sulphonated Quinophthalones, } Sulphonated Rosanilines, } Sulphonated Rhodamines, }</p>	$\begin{array}{c} R \\   \\ C = R \\   \\ R = N \equiv \end{array}$	<p>e.g., Spirit-soluble Quinoline Yellow. e.g., Water-soluble Quinoline Yellow.</p>
<p>The aqueous dyestuff solution is boiled with bleached cotton.</p>	<p>The cotton is not dyed.</p>	<p>Water soluble dyestuffs, reddish-violet, blue, or green, generally decolourised by potash lye, little affected by hydrochloric acid.</p>	<p>Red or violet dyestuffs giving fluorescent aqueous solutions; not affected by potash, or only slightly.</p>	<p>Yellow or orange dyestuffs giving more or less fluorescent aqueous solutions, dyeing silk, wool, and cotton directly.</p>	<p>Thiazol†</p>

\* The chromophores of the quinoline dyestuffs, Berberine and Flavaniline, are not as yet understood, they are probably compounds intermediate between the Auramines and Acridines.

† The thiazol dyestuffs are generally sulphonated, with the exception of Thioflavine T, which, although soluble in ether, dyes wool from an alkaline bath.

T A B L E E.

GROUP IV.—DYESTUFFS NOT REDUCED BY STANNOUS CHLORIDE AND HYDROCHLORIC ACID HAVING THE OXYQUINONE CARBON CHROMOPHORE O : R : C.

<p>Remains unchanged. <i>Non-amidated triphenylmethane dyestuffs</i>, generally soluble in water, and usually dyeing wool directly.</p>	<p>The dyestuff is dissolved or suspended in boiling water.</p>	<p>It does not dye wool directly. Generally insoluble in water, soluble in alcohol without fluorescence.</p>	<p><i>e.g., Aurine.</i></p> $\begin{array}{c} R \\ \diagdown \\ O \\ \diagup \\ R' \\ \diagdown \\ R=O \end{array}$
<p>The alcoholic solution of the dyestuff is treated with a few drops of a dilute solution of ferric chloride.</p>	<p>The alkaline solution is treated with an excess of hydrochloric acid.</p>	<p>Dyes wool directly. Generally soluble in water and alcohol to fluorescent solutions.</p>	<p><i>e.g., Eosin.</i></p> $\begin{array}{c} R' \\ \diagdown \\ C \\ \diagup \\ R' \\ \diagdown \\ R=O \end{array}$
<p>Turns green or olive-green. <i>Oxylketone dyestuffs</i> generally insoluble in water, dye fibres indirectly.</p>	<p>The alkaline solution is treated with 1 per cent. Potash lye.</p>	<p>Usually decolourised (with decomposition) especially on warming.</p>	<p><i>e.g., Alizarin Yellow A.</i></p> $\begin{array}{c} R \\ \diagdown \\ CO \\ \diagup \\ R \end{array}$
	<p>The original dyestuff is treated with Potash lye.</p>	<p>Gives an intense yellow without decomposition.</p>	<p><i>e.g., Quercetin.</i></p> $\begin{array}{c} R \\ \diagdown \\ CO \\ \diagup \\ C : C \\ \diagdown \\ R \end{array}$
	<p>Disolves with a red, reddish-violet, blue or green colour. <i>Diketones (Quinones)</i>.</p>	<p>The free acid is precipitated. Generally soluble in ether and dyeing the fibre indirectly.</p>	<p>{ Alizarin.</p>
	<p>Disolves with a red, reddish-violet, blue or green colour. <i>Diketones (Quinones)</i>.</p>	<p>The dyestuff remains in solution, is insoluble in ether and dyes wool directly.</p>	<p>{ Alizarin Red B.</p>

With the help of the foregoing tables, the dyestuff in question is assigned to the particular group or subdivision to which it belongs, and is then further identified by means of special tests in comparison with known colouring matters of the subdivision. It may be necessary to examine the solution spectroscopically or to decompose the dyestuff into simpler or more easily recognisable components. For example, the various phthaleïns may be recognised by boiling the solution with potash and zinc dust, and examining the filtrate after neutralisation with acetic acid, for bromine or iodine. An alternative method is to heat the dyestuff with lime to redness, dissolve in nitric acid, and examine the solution for the halogen. The detection of sulphur to distinguish, for example, thiazines from oxazines is effected by fusing the dyestuff with potassium nitrate, dissolving, and examining the filtrate for sulphates. If the dyestuff be reducible by stannous chloride, the solution is freed from tin by sulphuretted hydrogen, and the filtrate is examined for the reduction product. Thus Picric acid yields triaminophenol, which on treatment with ferric chloride gives blue aminodi-iminophenol. Azo-dyestuffs on reduction give at least two primary amines, which frequently can be separated by ether. The reduced solution, after removing the tin, is treated with an excess of potash, and extracted with ether. The unsulphonated amines are removed, whilst the sulphonated ones remain in the aqueous solution. The latter can be recognised by giving characteristic azo-compounds with certain diazo-derivatives. For example, sulphanilic acid, obtained by reducing Naphthol orange, gives, when combined with tetrazodiphenyl chloride, a yellow tetrazo-dyestuff; naphthionic acid gives Congo red, and certain hydroxysulphonated amines, such as 2:1':3',  $C_{10}H_7 \cdot NH_2 \cdot OH \cdot SO_3H$ , give a violet colour (Diamine black R, &c.). The presence of a *p*-diamine is recognised by the thiazine reaction (ferric chloride and hydrochloric acid in presence of sulphuretted hydrogen), and in non-amidated dyestuffs this reaction affords a means of distinguishing between mono- and disazo-dyestuffs. It is also possible to decide in this case whether a sulphonic acid group is in the side or middle ring, since in the former case a thiazine is formed which, in presence of potash, can be extracted by ether, whereas a sulphonated thiazine remains in the aqueous solution.

H. Huntington\* has published a series of tables for the recognition of dyes, in which the reactions made use of are:—

1. Reaction with concentrated sulphuric acid.
2. Change on diluting this solution.
3. Addition of HCl to aqueous solution of the dye.
4. Addition of NaOH to aqueous solution of the dye.

These tests have been previously used by Schultz and Julius† and Green,‡ but are here arranged in a form very convenient for use.

\* *Year Book for Colourists and Dyers*, vol. i., 1898.

† *Tabellarische Übersicht der künstlichen Farbstoffe*.

‡ English edition and extension of the above. See also Gulinow, *Zeit. Farben. Ind.*, 1906, p. 537; *Journ. Soc. Chem. Ind.*, 1906, p. 1007.

## EXAMINATION AND ANALYSIS OF TEXTILE FABRICS.

The characteristics of the various fibres have been given under the headings *Cotton, Linen, &c., Wool, and Silk* (pp. 21 to 72). The fibres are best distinguished from each other by means of the microscope. Wool and silk are easily distinguished from cotton by drawing out a thread and setting it on fire. The animal fibres shrivel up and leave a shining tumefied, difficultly combustible cinder. The smoke smells like burnt horn, and turns turmeric brown. The vegetable fibres leave a cinder having the form of the original thread, and only a small quantity of ash; while they burn with a smoke which has an empyreumatic smell, and reddens litmus. Wool and silk are also easily distinguished from cotton and linen by the yellow colour which they assume when treated with nitric or picric acid, by which the vegetable fibres are not coloured.

Wool and silk also dissolve by boiling with potash or soda lye of specific gravity 1.045, whereas the vegetable fibres remain unchanged. When treated with ammonio-cupric oxide solution, cotton, linen, and silk dissolve, while wool is insoluble.

Wool and silk can be distinguished from each other by a solution of plumbite of soda, which can be prepared by adding caustic soda to acetate of lead until the resulting precipitate redissolves. Both wool and hair when treated with this solution turn brown, in consequence of the sulphur which they contain, forming dark lead sulphide; while silk which is free from sulphur remains unchanged. It is obvious that this reaction is useful only when the fabric does not contain, besides wool, a notable quantity of stoved silk.

Grothe gives the following as the best methods of distinguishing wool and silk\* :—

(1) Wool, cautiously heated to 130° C., gives off the odour of carbon disulphide and ammonia, assumes a golden-yellow colour and curls up, while silk becomes coloured only at 140° to 145° C., and does not curl up.

(2) When the fibres, moistened with potash lye, are dipped in a solution of cupric sulphate, and then exposed to the air, the wool quickly turns brown in consequence of the formation of cupric sulphide, whereas the silk remains unchanged.

(3) On mixing the solution of wool in caustic potash with tartaric acid, and then with cupric sulphate, a large quantity of cupric sulphide is formed, and the filtered liquid exhibits a dark brown-red colour. Silk treated in the same manner yields a somewhat viscid solution, having a fine violet colour.

Animal fibres, when heated with Millon's reagent (mercuric and mercurous nitrate), turn red. With vegetable fibres this is not the case.

The vegetable fibres (cellulose), as well as silk, are readily dissolved in an ammoniacal solution of copper oxide (prepared, according to Peligot, by dissolving copper filings in a small quantity of ammonia), and the former may be precipitated by a number of salts, as well as by sugar or gum, whereas silk can only be separated by means of weak acids.

According to Schlossberger, an ammoniacal solution of protoxide of nickel very easily dissolves silk without attacking cotton.

Liebermann has proposed a very sensitive reaction for the detection of vegetable fibres among animal fibres. For this purpose a saturated solution of Magenta is prepared, to which caustic potash is added until the solution becomes colourless. The filtered colourless portion of this solution is used for the examination of fibres. The fabric to be tested is dipped for some moments

\* *Zeitschr. Analyt. Chem.*, vol. iii., p. 153.

into the liquid, and, after withdrawal, well washed with water. The effect of this treatment is that the wool or silk is coloured red, whilst the cotton fibres remain altogether colourless.

Persoz finds that silk dissolves readily in a hot solution of zinc chloride of  $142^{\circ}$  Tw.

Rémont has devised the following method:—The sample is boiled for fifteen minutes in a 3 per cent. solution of hydrochloric acid, then washed and dried. The threads of the warp are then separated as far as possible from those of the weft, and examined separately, as mentioned below. A thread is burnt. There is given off a smell like burning horn, and a thread, heated with a fragment of caustic soda, evolves ammonia. In this case some threads are plunged into boiling basic zinc chloride solution. If they dissolve completely the threads are *silk*. If on adding to this solution hydrochloric acid there is a copious flocculent precipitation, the threads are silk mixed with wool or vegetable fibres. If nothing dissolves in zinc chloride the threads are plunged into a boiling 5 per cent. solution of soda. If they dissolve completely wool is present; if partially, wool and cotton. If no odour of burnt horn is given off, the threads consist of vegetable fibres. These results may be confirmed by means of the microscope.

For the **Quantitative Examination**, if the preliminary tests show the presence of silk, wool, and cotton, four swatches weighing each 4 grms. are taken, one of which is laid aside.

The swatches are boiled for fifteen minutes in a 3 per cent. solution of hydrochloric acid. If the liquid is deeply coloured it is decanted, and the boiling is repeated with a fresh quantity of acid. The pieces of cloth are then well washed and dried by wringing them in a piece of linen, and one of them is put aside. In this manner the fabric is freed from size and dressing, and the dye is more or less removed. The colour is thus easily removed from cotton, less readily from wool, and very incompletely from silk. When the latter material is dyed light shades by means of coal-tar colours the weight of the dye is trifling, and may be neglected. It is not the same if the silk is dyed deep colours, and especially black. An approximate idea of the weighting retained by the tissue may be got by afterwards incinerating a weighed portion of the boiled swatch. If the proportion of oxide of iron remaining is slight, it may be overlooked, but if it reaches 5 to 10 per cent. calculated on the weight of the silk in the cloth it must be taken into account. Two of the pieces, after the treatment with acid and washing, are immersed for one or two minutes in a boiling solution of basic chloride of zinc of 1.72 specific gravity. This is prepared by heating 100 parts of zinc chloride and 4 parts of zinc oxide in 85 parts of water until dissolved. The patterns are allowed to drain and then placed in water, which removes the greater portion of the zinc salt. They are then washed with acidulated water, and eventually in pure water, until the wash water no longer gives a precipitate with ammonium-hydrogen sulphide. By wringing the patterns after each immersion in a piece of linen the operation is accelerated, and the silk is thus completely removed. One of the patterns is then laid aside. In order to separate the wool, the remaining swatch is gently boiled for a quarter of an hour in a 2 per cent. solution of caustic soda, the loss of water by evaporation being continually replaced by boiling water. In washing and drying the residue it must not be rubbed, lest losses be occasioned by the breaking of the fibres.

The four patterns are then dried in a water oven for an hour, and, after taking out, exposed to the air in the same place where the sample was originally kept. The following day the pieces are weighed. The first piece should weigh 4 grms., any difference not exceeding 0.005 grm. may

be neglected, but any greater difference must be taken into account. The difference in weight between the first and second patterns gives *size and dressing*; that between the second and third represents the weight of *silk*; that between the third and fourth the weight of *wool*; whilst the weight of the fourth gives the amount of *vegetable fibre* present. Since the vegetable fibre is attacked somewhat by the caustic soda, it is usual to make an allowance of 5 per cent.; consequently on adding to the fourth swatch 5 per cent. of its weight we obtain the weight of cotton.

Fabrics and yarn, composed of two fibres (cotton and wool, wool and silk, cotton and silk), are much more common than those with three, when, of course, one of the above operations is omitted.

In many cases the cotton and wool in mixed goods may be determined by carefully separating the weft and the warp threads and weighing the fibres thus obtained.

As is well known, cellulose, when treated with acids, is partly changed into sugar, and thus gives indirectly the sugar reaction with linen, cotton, hemp, jute, &c. Starting from this fact, and from the property of various kinds of sugar producing fine colourings with  $\alpha$ -naphthol or thymol and sulphuric acid, Molisch \* has devised a method of distinguishing vegetable from animal fibres, which in precision leaves nothing to be desired. To avoid all error, the sample under examination must first be boiled several times in water, considering that for some fabrics gum is used as sizing, for others *Plantago psyllium* or saccharine substances, which, with naphthol and sulphuric acid, produce coloured reactions. If a wool is to be assayed care must be taken that it does not contain burrs, &c. The method of proceeding is then as follows:—About 0.01 grm. of fibres, well boiled and washed in plenty of water, is put into a test tube, two drops of a 20 per cent. alcoholic solution of  $\alpha$ -naphthol added, and then well shaken with concentrated sulphuric acid. If the sample contains *vegetable fibres* the latter are rapidly dissolved, and the liquid, after being shaken, assumes a deep violet colour. If, on the contrary, the fibres are of animal origin, the liquid is coloured a more or less intense yellow, or even brown. If under the same conditions thymol, instead of naphthol, is employed, a colouration between cinnabar and carmine is obtained. Beta-naphthol does not give these reactions, and  $\alpha$ -naphthol is preferred to thymol, because the reaction is better. It is to be observed that the colouring matters do not in any way interfere with this reaction. By noticing, in the course of the reaction, the solubility of the different fibres in sulphuric acid, the character of the fibres contained in the fabric may be ascertained. If, for instance, no colouring is produced, which is a sign that the fabric is composed of animal fibres only, the solubility of the latter indicates their origin; silk dissolves very rapidly and completely, while wool is not dissolved at all. If a colouration takes place, and if the fibres are dissolved completely, the fabric will be of vegetable origin, and may contain, besides, fibres of silk. A colouring, accompanied by an incomplete solution of fibres, indicates that the fabric contains wool mixed with vegetable fibres.

Although these reactions with  $\alpha$ -naphthol are very simple, they cannot by themselves suffice for the assaying of the fabrics, and should be employed only in concurrence with other tests described above.

According to A. Lidoff, *raw silk* dissolves rapidly in melted oxalic acid, *cellulose* dissolves but slowly, while *wool* does not dissolve at all.

For separating *silk* from *cotton* the following solution may be used:—

15 grms. of copper sulphate are dissolved in 150 c.c. of water, 10 grms. of pure glycerin are added, and just sufficient caustic soda to redissolve the precipitate which is at first formed.

\* *Ding. Polytec. Journ.*, No. 3, vol. cclxi.

If the fabric (plush) be heated for twenty minutes in this solution the *silk* is completely dissolved; the *cotton* loses about 1 per cent. of its weight in the process. *Wool* is dissolved to a considerable extent by the copper solution mentioned, hence this method cannot be used in the presence of wool.

F. W. Richardson\* uses for dissolving *silk* a solution of nickel hydrate prepared as follows:—25 grms. of crystallised nickel sulphate are dissolved in about 500 c.c. of water, and the nickel completely precipitated as hydrate by caustic soda; the hydrate is thoroughly washed with water, then rinsed into a 250 c.c. flask with 125 c.c. of water; the flask is then filled to the mark with 0.880 ammonia, and well shaken.

This solution dissolves *silk* from fabrics other than plush in two to three minutes in the cold, the losses of *cotton* and *wool* by this treatment being less than 0.5 per cent. In order to dissolve *silk* from *plush* ten minutes' boiling with a reflux condenser is required; in this manner *cotton* loses nearly 1 per cent. For the *analysis of plush* it is best to boil the fabric with basic zinc chloride (1.72 sp. gr.), wash with dilute acid and water as mentioned above, dry and weigh the *cotton*. It is advisable to boil some dyed fabrics with methylated spirit, and finally with ether, to remove certain dyes and oleaginous substances, before treating as above.

*Tussur silk*, and other wild silks, behave with various reagents differently to mulberry silk. *Ordinary silk* is soon dissolved in a 10 per cent. solution of boiling caustic soda, but *Tussur silk* requires a considerable time.

*Tussur silk* is only partially dissolved by cold concentrated hydrochloric acid (sp. gr. 1.16), even on standing forty-eight hours, whilst *ordinary silk* dissolves almost instantly. The zinc chloride solution mentioned above, which dissolves mulberry silk readily, only dissolves *Tussur silk* after a considerable time, and then incompletely. Hoehnel gives the following method for the qualitative and quantitative determination of the different silk fibres. If a sample of mulberry silk is plunged into a solution of chromic acid saturated in the cold and then diluted with an equal volume of water and boiled for one minute, the silk dissolves completely. Wild silks remain apparently unaltered after boiling for two or three minutes. *Wool* behaves in this solution like mulberry silk.

In the analysis of all fabrics it is best to take the exact weight of the substance when dried to constant weight, using a stoppered tube both before and at the end of the various treatments, as the fibres are more or less hygroscopic.

*Weighted silks* are tested as follows by J. Carter Bell:†—5 grms. are dried for the estimation of the *moisture*, then extracted with ether, alcohol, and water, weighing between each solvent. This will give the quantities of *oil*, *soap*, *sugar*, and similar compounds added for weighting purposes. Half of the sample is next treated with hydrochloric acid diluted with two volumes of water; the silk is then dried at 230° F. It can then be reduced to powder, which can be mixed with soda lime, and the combustion for nitrogen carried out as usual.

*Tin*, which is largely used for weighting silks, is detected by heating the silk in strong hydrochloric acid, added in quantity to effect solution, then diluting with water, and passing a current of sulphuretted hydrogen through the solution, when the tin is precipitated as sulphide, and may be further tested in the usual manner.

The *ash* of a genuine silk is about 0.5 per cent., while *Tussur silk* gives 8 per cent. of ash.

The standard for the amount of nitrogen is pure boiled off silk, dried at the ordinary temperature, which contains 18 per cent. nitrogen.

\* *Journ. Soc. Chem. Ind.*, 1893, p. 430.

† *Ibid.*, 1897, p. 303.

An interesting paper on the "Estimation of weighting on silks" is given by J. Persoz in the *Revue Générale des Matières Colorantes*,\* 1906, p. 322.

Artificial silk may be distinguished from natural silk by its property of not being dyed by acid colours (see also p. 71).

The following methods of distinguishing artificial or collodion silk from natural silk are recommended by P. Truchot:—†

1. The density of collodion silk is 1.490, that of silk 1.357 to 1.37.

2. When ignited, collodion silk burns without the emission of any acid gases or smell.

3. When treated with Schweitzer's reagent (*q.v.*), collodion silk and silk both swell considerably before dissolving. On the addition of water or hydrochloric acid to the solution obtained from the collodion silk, a white precipitate of cellulose is produced.

4. Collodion silk dissolves in concentrated sulphuric acid with a deep yellow colour, which, on the addition of diphenylamine or of brucine, turns respectively dark blue or red. These colour-changes are very characteristic, and are due to the presence in the fibre of collodion silk which has escaped reduction by the compounds with which it has been treated. The test may be made without dissolving the fibre, the latter being simply immersed in a solution of diphenylamine sulphate, when it becomes coloured dark blue, natural silk when similarly treated remaining colourless.

5. A simple test for collodion silk consists in separating the fibres, moistening them with water, and determining their tenacity. The fibres of collodion silk, when moistened, become very weak, whilst silk, whether moist or dry, withstands great tensile strain.

**Estimation of Water.**—The conditioning of textile fibres and fabrics has been already referred to under *Wool* and *Silk* (pp. 49 and 62); but it is frequently necessary to operate upon smaller samples of material than are suitable for the apparatus in general use for that purpose. As a rule, it suffices to dry 2 to 3 grms. of the material in a large stoppered tube in the steam-bath until of constant weight. This method generally takes several hours to obtain exact results. The following method, devised by Rawson, gives very good results:—5 to 10 grms. of the yarn or cloth are weighed out and introduced into a thin glass tube of special construction. The body of the tube is about 6 inches in length and 1 inch in diameter. One end is fitted with a ground glass stopper (as in an ordinary filter tube) and the other is connected with a short piece of open tubing about  $\frac{1}{4}$  inch in diameter and 2 inches in length. The stopper is removed and the tube inserted by means of a cork into a tubular water-bath. A current of dry air is drawn through the tube by means of an aspirator, whilst the water in the bath is kept boiling. At the end of forty-five minutes the glass tube with its contents is removed from the bath, the stopper is inserted and the small open end connected by means of a short piece of india-rubber tubing, to a calcium chloride tube. When cold, the tube containing the dry fibre is weighed, the loss in weight being water. If desired, the tube may be again heated in a current of air, but it is seldom that a further loss takes place. The operation is completed in a shorter time if a temperature of 105° to 110° be employed instead of that of boiling water. This temperature may be conveniently obtained by using a mixture of glycerin and water. The bath (especially if glycerin or any other substance in addition to water be used) should be provided with an upright condenser. The bath can be made to accommodate half a dozen or more tubes, if desired.

**Estimation of Oil.**—Oil and grease in fabrics, &c., are most conveniently determined by extraction with ether or petroleum ether in a Soxhlet's

\* *Abs. Journ. Soc. Dyers and Col.*, 1906, p. 21.

† *Journ. Soc. Chem. Ind.*, 1898, p. 186.



apparatus. Before using ether, it is necessary to purify that solvent. Small quantities of alcohol if present in the ether will be liable to dissolve off the dye, hence the removal of alcohol from the ether is sometimes advisable. This is effected by shaking out with water. The ethereal layer after separation is dried by allowing it to stand in contact with a little solid calcium chloride and then filtering. In any case the ether should be distilled from a water-bath, the residue in the distilling flask being rejected.

A. Jawalovski \* condemns the use of ether for this purpose, since in the first place it does not dissolve some of the constituents of mineral oils which are often used (mixed with vegetable oil) for oiling wool. Ether is also more liable than petroleum ether to dissolve out soap.

Whichever solvent be made use of, 2 to 5 grms. of the material are taken and introduced into the body of the tube. The lower extremity of the apparatus is connected with a small wide-mouthed flask (previously weighed dry) containing about 60 c.c. of the solvent, and the upper end is connected with an inverted condenser. The flask is arranged to rest on a water-bath, under which is placed a small flame. The heat is so regulated that the ether distils and syphons over into the flask at the rate of about twelve times per hour. When the extraction is complete, the ether is recovered from the extracted liquid by evaporation, and the flask containing the extract is dried for half an hour in a water-oven, allowed to cool and weighed. No further loss should ensue on heating for fifteen minutes longer in the oven.

Estimation of Mineral Matter (*Metallic oxides as mordants, &c.*).—The total mineral matter is determined by burning 5 to 10 grms. of the material in small portions at a time in a platinum dish and igniting until all the carbon has disappeared. As the ash is usually very light, great care must be taken to prevent any portions being carried away by air currents. The dish, on cooling, is then weighed.

The Qualitative Analysis may be made on small amounts of the fabric in a similar manner, the ash free from carbon being treated as follows:—

*Chrome Mordants.*—Ash, yellowish- or brownish-green. Add a little potassium chlorate and fuse; a bright yellow mass is obtained. If dissolved in water and acetic acid and acetate of lead added a yellow precipitate is obtained, confirming the presence of chromium. If a trace of chromium is present it may be detected by means of a borax bead, which acquires a green colour in the presence of chromium.

*Iron Mordants.*—Ash, reddish-brown colour. Dissolve in hydrochloric acid, add potassium ferrocyanide; a blue precipitate indicates iron.

*Copper Mordants* (usually occur in combination with iron and sometimes with chrome).—Dissolve the ash in hydrochloric acid, add a slight excess of ammonia and filter. If much copper is present the filtrate will be blue. Smaller quantities are detected by adding acetic acid and potassium ferrocyanide, which produce a reddish-brown precipitate or colour.

*Aluminium Mordants.*—Ash, white. Dissolve in hydrochloric acid and add ammonia, which gives a white precipitate in presence of alumina. Confirm by heating on charcoal with cobalt nitrate; a blue mass is thus obtained.

*Tin Mordants.*—Ash, white; yellowish when hot. Globules of tin are obtained by heating on charcoal; small quantities detected by the red colour imparted to a borax bead containing a trace of oxide of copper when heated in the reducing flame.

D. Paterson† finds that tin in woollen fabrics may be detected by carefully examining the strongly heated ash of the material. If tin is present the ash assumes a characteristic dark indigo-blue iridescence in small patches, with here and there spots of white.

\* *Journ. Soc. Dyers and Col.*, 1886, p. 89.

† *Ibid.*, 1906, p. 189.

**The Quantitative Analysis of the Ash of Fabrics.—***Estimation of Chromium.*  
 —The ash from about 5 grms. of material is mixed with ten to twelve times its weight of a mixture of 2 parts of potassium chlorate and 3 parts of sodium carbonate and fused for twenty minutes in a platinum crucible. On cooling, the mass is treated with hot water and filtered, the residue being well washed with hot water. The filtrate and washings are poured into a porcelain basin, treated with considerable excess of sulphuric acid and a known weight (in slight excess) of pure ferrous ammonium sulphate. The excess of ferrous iron is then titrated with  $\frac{N}{10}$  potassium bichromate (*v. Potassium Bichromate, Analysis of*). One part of ferrous ammonium sulphate consumed (after deducting excess) =  $0.065 \text{ Cr}_2\text{O}_3$  or  $0.0854 \text{ CrO}_3$ .

*Estimation of Iron and Copper.*—If chromium is present the residue, after fusing and treating with water, is dissolved in hydrochloric acid; in some cases the addition of a little nitric acid is also necessary. The acid solution is diluted with a little water and an excess of ammonia added. The ferric hydroxide is collected on a small filter, washed a little, re-dissolved in hydrochloric acid and titrated colorimetrically, either with potassium ferrocyanide or thiocyanate (*v. Water Analysis*).

The copper in the filtrate and washings is estimated by "colour titration" in the following manner:—The ammonia is carefully neutralised with acetic acid (a very slight excess of acetic acid is allowable) and the liquid made up to a known volume. A measured volume of the neutralised solution is run into a Nessler glass tube, half a c.c. of a 5 per cent. solution of potassium ferrocyanide is added, and the liquid diluted to 100 c.c. The depth of shade produced is compared with that given by a standard solution of copper treated in exactly the same manner in another Nessler tube. The copper solution is prepared by dissolving 0.393 gm. of pure crystallised copper sulphate in a litre of water. 1 c.c. of this solution = 0.0001 gm. of Cu.

For the estimation of chromium and iron by titanous chloride see S. B. Jatar, *Journ. Soc. Chem. Ind.*, 1908, p. 673, and for the estimation of copper, chromium, and iron in admixture, see E. Hibbert, *Journ. Soc. Chem. Ind.*, 1909, p. 190.

**Estimation of Colouring Matters on the Fibre.**—Until recently the only colouring matter which could with any pretence to accuracy be estimated on the fibre was Indigo. Methods for this determination have already been given under *Indigo*, p. 329. Since that article was written Knecht\* has introduced a new method for the estimation of indigo in dyed cotton which has given very good results. The method is based on two well-known facts, viz. :—(1) That cellulose readily and completely dissolves in 80 per cent. sulphuric acid at 35° to 40° C.; and (2) that indigotin is also soluble in sulphuric acid of this strength, forming a sulphate which, when diluted with water, dissociates with separation of the whole of the indigotin as such. About 4 grms. of the sample of dyed cotton (more or less, according to the depth of shade) are cut up into small pieces and dissolved into 25 c.c. of 80 per cent. sulphuric acid at a temperature of about 40° C. The operation is carried out in a small porcelain beaker, and solution takes place after stirring for about ten minutes. The contents of the beaker are diluted to about 120 c.c. with water and boiled for a few minutes, when the precipitated indigotin becomes granular, and can be rapidly filtered. A Gooch crucible, containing a little quartz, covered with a layer of finely-divided silica, is used for the filtration. After washing, the Gooch, with its contents, is dried at 110° to 120° C., and the indigotin dissolved in a little concentrated sulphuric acid. The solution is diluted to a given bulk, and an aliquot part titrated with either titanous chloride or potassium permanganate (see pp. 819 and 822). For the estimation of indigo on wool

\* *Journ. Soc. Dyers and Col.*, 1909, pp. 135, 160.

extraction with phenol as proposed by Brandt for indigo (see p. 824) can be recommended.

Schaposchnikoff and Minajeff\* propose to estimate such dyes as Diamine blue 3 B on cotton by fusing the fabric with saltpetre and estimating the sulphuric acid thus formed by precipitation with barium chloride. Knowing the amount of sulphur contained in the dyestuff, the amount of the latter is then easily calculated. Knecht† has found that many of the direct cotton colours can be estimated direct by treating the dyed material with an excess of titanous chloride and titrating back with iron alum. If any active chlorine is present on the fibre, this can be readily removed by boiling for five minutes with dilute hydrochloric acid. For the operation 5 grms. of the dyed cotton are put into a wide-mouthed flask and boiled with dilute hydrochloric acid, whilst carbon dioxide is passed in. An excess of standard titanous chloride (see p. 793) is then run in and the flask heated until the colour has disappeared, when it is rapidly cooled in running water and the excess of titanous chloride titrated with standard iron alum and potassium thiocyanate as indicator. During the whole process the CO<sub>2</sub> current must not be interrupted. Examples are given in the paper referred to as Benzopurpurin 4 B, Chrysophenine, Brilliant yellow, and Erika B.

Methylene blue on cotton may also be estimated in the same way.

Detection and Estimation of Arsenic in Textile Fabrics, &c.—In the first place it is necessary to obtain the arsenic in a soluble form, free from organic matter. Fresenius and Hintz‡ take 25 grms. of fabric, cut it up, and introduce it into a stoppered retort of about 500 c.c. capacity. The neck of the retort is bent in an obtuse angle, and so placed that the portion near the bulb is vertical. The neck is connected with a condenser, to which a receiver of 700 to 800 c.c. capacity is attached. The receiver contains 200 c.c. of water. 250 c.c. of hydrochloric acid (specific gravity 1.19) are poured into the retort, and after the cut up fabric has been digested for an hour, 5 c.c. of a cold saturated solution of ferrous chloride are added, and the liquid distilled down to a small bulk. The distillate contains the arsenic as arsenious acid. In certain cases it would appear that the whole of the arsenic is not given off by distillation, and it is, therefore, preferable for quantitative work to destroy the organic matter by nitric acid or a mixture of nitric and sulphuric acids. Knecht recommends§ heating the material with nitric acid (specific gravity 1.5) in sealed tubes at 250° C. for two hours. The excess of nitric acid is then driven off and the arsenic estimated by the Marsh process as indicated by Sanger.|| The organic matter may also be destroyed by nitric and sulphuric acids, as described by Chittenden and Donaldson.¶

Thomson and Shenton\*\* employ a similar process for destroying the organic matter in beers, foods, &c., previous to estimating the arsenic. In the case of textile fabrics the following method can be recommended:—About 5 grms. of the material is cut up and introduced into a hot mixture of 20 c.c. pure strong nitric acid and 5 c.c. pure concentrated sulphuric acid. The material dissolves and the liquid is boiled down until it blackens, when more nitric acid is added in small portions and the concentration continued until fumes of sulphuric acid are evolved. On cooling, water is added, and the solution boiled down until the liquid is quite free from nitric and nitrous acids.

\* *Journ. Soc. Dyers and Col.*, 1904, p. 181.

† *Ibid.*, 1905, p. 3.

‡ *Zeit. Anal. Chem.*, xxvii., p. 179; *Journ. Soc. Chem. Ind.*, 1888, p. 456.

§ *Journ. Soc. Chem. Ind.*, 1901, p. 207.

|| *Amer. Chem. Journ.*, 1891, p. 431; *Journ. Soc. Chem. Ind.*, 1892, p. 370.

¶ *Chem. News*, 1881, p. 21.

\*\* *Journ. Soc. Chem. Ind.*, 1901, p. 205. See also Richardson, *Journ. Soc. Chem. Ind.*, 1902, p. 902, and Report of Arsenic Committee, *Journ. Soc. Chem. Ind.*, 1902, p. 95.

Having obtained the arsenic in solution by one or other of the above-mentioned methods, the liquid is ready to be treated in the Marsh-Berzelius apparatus, of which there are many patterns.

*Marsh-Berzelius Test.*—About 25 grms. of pure zinc rods are introduced into a flask of a capacity of 250 c.c., having a horizontal side tube attached to the neck. This is connected to a calcium chloride tube, into which is fixed a piece of hard glass tubing about 12 inches in length and a quarter inch in diameter. The drying tube also contains a piece of cotton wool saturated with lead acetate and dried to absorb any hydrogen sulphide. The hard glass tube is drawn out near the end and bent upwards. The flask is provided with a tapped funnel, through which a little dilute pure hydrochloric acid is poured, and allowed to flow on to the zinc. When the air has been *completely* driven out of the apparatus, the jet is lighted and the hard glass tube (protected with wire gauze) heated to redness for a space of 6 or 8 inches by means of a small furnace of four or five Bunsen burners. An aliquot part of the solution containing the arsenic is poured into the funnel and allowed to drop regularly into the flask at the rate of about 1 c.c. per minute. Arseniuretted hydrogen ( $\text{AsH}_3$ ) is formed, which, on passing through the red-hot tube with excess of hydrogen, is decomposed and arsenic is deposited. If the amount of arsenic is considerable, a space of 2 or 3 inches should be left between the heated portion and the drawn-out part of the tube. If very small, the tube should be heated close to the drawn-out part so that the arsenic may be deposited in the narrow portion. When the acid liquid containing the arsenic has passed into the flask, 10 to 20 c.c. of pure hydrochloric acid are added and allowed to slowly flow in as before. The tube is then allowed to cool, when the portion containing the deposit of arsenic is cut off with a sharp file and carefully weighed on a delicate balance. The arsenic is then removed by simply heating the tube, which, after cooling, is again weighed. The difference between the two weighings gives the amount of arsenic present in the solution. In many cases the arsenic mirror may be too small to weigh, and yet it may represent a considerable amount (comparatively speaking) of arsenic. In such cases the amount of arsenic may be estimated by making experiments with known quantities (very small) of arsenic, and comparing the mirrors obtained. Before commencing the examination for arsenic, it is absolutely necessary to make blank experiments with all the substances used in order to ascertain whether they are quite free from arsenic or not.

The determination of small quantities of arsenic has recently received considerable attention from chemists, and many papers have been read on the subject. The following references may be given:—*Journal of the Chemical Society (Trans.)*, 1903 (lxxxiii.), p. 974; *Journal of the Society of Chemical Industry*, 1901, pp. 188, 204, 208; 1902, pp. 93, 901; 1903, p. 964; 1904, pp. 159, 177, 799; 1907, pp. 1115, 1226.

*Identification of Dyestuffs on the Fibre.*—The recognition of the colouring matters which have been employed in dyeing is frequently a matter of considerable difficulty; especially is this the case when two or more dyes have been used in producing the shade. Tables have been prepared showing the characteristic changes which occur with various reagents of a great number of colouring matters, but when several dyes are used, as is frequently the case in practice, the tables in themselves cannot be relied upon. A very small quantity of certain colours, giving striking reactions with acids, alkalies, &c., is sufficient to altogether obscure the slight changes which take place with other colouring matters.

The general plan adopted in the detection of dyes is, if possible, to determine in the first place the group or groups of colouring matter to which those present belong, and this is greatly facilitated by the investigator's

knowledge and experience, which frequently enable him at once to fix upon the probable group. For example, no dyeworks chemist would expect a bright red on *cotton* to be dyed with cochineal, but it might be either Turkey-red, a direct cotton colour, a developed azo-dye, or a basic dye. On the other hand, a bright red on *wool* might be an acid, a direct, a basic, an alizarin, or cochineal dye, but would probably not be a developed azo-compound. The first step should usually be to determine whether a metallic mordant has been employed, since this greatly narrows the field of inquiry. For example, if a bright red on *wool* was found to contain *chromium* as mordant, this would at once point to the presence of an azo-mordant dye (Cloth red, &c.). If *aluminium* was found, Alizarin would be the most likely dye, while *tin* would probably indicate cochineal.

Methods for detecting the principal mordants which may occur on dyed fabrics are given on p. 864.

Too much reliance must not, however, be placed on the result of the examination for mordants, because certain mordant dyes—*e.g.*, *Nitro-alizarin*—are occasionally employed without mordant; and, on the other hand, metallic oxides may be met with both on white material and on cloth or yarn dyed with non-mordant dyes; metals being employed, for example, in rendering wool unshrinkable and in waterproofing processes. In most cases, however, the presence of a metal in the ash obtained on burning the material affords a strong presumption that the colouring matters used belong to the group of mordant dyes, and further experiment should be first made on this assumption.

If the dyestuff under examination is not a mordant dye, an endeavour should be made to determine to what group of colouring matter it does belong, and this may usually be done by the use of acid or alkaline reducing agents. In this way the colouring matters are divided into the following groups:—

1. *Decolourised, but quickly reappears on exposure to air.*—Azines, oxazines, thiazines, acridines, sulphide colours, indigo, and other vat dyes.
2. *Decolourised, not restored by air, but by oxidising agents.*—Rosaniline dyes and phthaleines (Eosines).
3. *Permanently decolourised.*—Azo-dyes, nitro- and nitroso-compounds.
4. *Colour unaffected.*—Alizarin dyes, Primuline, and a few others.

Having determined the group to which the colour belongs, the field of enquiry is much narrowed, and before proceeding further small pieces of wool, cotton, or silk should be dyed with the suspected colouring matter which experience suggests as being the most likely to be present. The two pieces of dyed material—that dyed with the known colouring matter and the sample—are then tested side by side with the same reagents under identical conditions.

Gardner\* recommends the following list of reagents, to be applied in the order given:—

1. Boiling water; if any colour removed, boil again with fresh water.
2. Boiling alcohol.
3. Nitric acid, specific gravity 1.32 (cold).
4. Hydrochloric acid, specific gravity 1.16 (cold).
5. Sulphuric acid, conc. (cold).
6. Sulphuric acid, 5 c.c. per litre (boiling); if any colour removed, repeat.
7. Sulphuric acid, 50 c.c. per litre (boiling); if any colour removed, repeat.
8. Caustic soda, 15 per cent. solution (cold).

\* *A Dictionary of Dyes, &c.*, Rawson, Gardner, and Laycock, p. 109.

9. Ammonia, specific gravity 0·88 (cold).
10. Borax, 10 grms. per litre (boiling).
11. Chromic acid solution (boiling)—
 

10 grms. potassium bichromate	}	per litre.
3·5 grms. sulphuric acid		
(Acid oxidising agent.)		
12. Sodium peroxide, 1 grm.
 

Magnesium sulphate, 2·4 grms.	}	per litre.
(Alkaline oxidising agent.)		

 Apply at 50° C. ; if no action, boil.
13. Bleaching powder solution, specific gravity 1·04 (cold).
14. Sulphurous acid (boiling)—equal parts of—
 

(a) 10 grms. sodium bisulphite, specific gravity 1·3,	}	per litre.
(b) 3·5 grms. sulphuric acid		
(Acid reducing agent.)		
15. Stannous chloride solution—
 

20 grms. stannous chloride	}	per litre.
100 c.c. hydrochloric acid, specific gravity 1·16,		
(Acid reducing agent.)		
Apply cold ; if no action, boil.		
16. Ammonium sulphide solution, 100 grms. per litre.
 

(Alkaline reducing agent).
17. Nitrous acid (boiling)—equal parts—
 

(a) 5 grms. sodium nitrite	}	per litre.
(b) 3·5 grms. sulphuric acid		
18. Apply test 17 cold, then wash and steep the material in a solution of beta-naphthol, 5 grms. per litre.

Knecht\* finds a dilute solution of titanous chloride to be a valuable reducing agent in the examination of dyes in the fibre. It possesses certain advantages over stannous chloride and sodium hydrosulphite. Dyed on cotton, the azo-dyes are almost instantly discharged when boiled with a dilute solution of titanous chloride. Primuline red is discharged to yellow. Paranitraniline red is discharged white on boiling for about two minutes, whereas alpha-naphthylamine claret requires a longer time for its destruction. Primuline (undeveloped) and all allied colouring matters are not affected even on boiling for some time. In the case of basic colours dyed on tannic acid and antimony mordant the colour is, in most cases, completely destroyed ; the fibre remaining a dull yellow to brown in consequence of the formation of tannate of titanium. Except in a few cases (Rhodamine, Thioflavine T), the colour is not afterwards restored by washing in running water or by treatment with dilute hydrogen peroxide. The sulphide colours, on boiling with dilute titanous chloride, rapidly turn brown or drab, but the original colour is restored on washing with water or by immersion in dilute peroxide of hydrogen. Aniline black behaves in a similar manner. Indigo is at first converted into indigo white as with hydrosulphite, but on continuing to boil with titanous chloride the reduction goes still further and the indigo is completely destroyed. This property enables one to detect sulphide colours on cotton in the presence of indigo. Prussian blue is almost instantly decolourised by titanous chloride, but the colour is restored by washing and exposure to air. Iron buff is quickly reduced and removed from the fibre as a ferrous salt.

Titanous chloride may also serve in some cases for the identification of dyestuffs in admixture with each other by virtue of its selective action as a reducing

\* *Journ. Soc. Dyers and Col.*, 1904, p. 98.

agent. Thus, if cotton dyed green with a mixture of Diamine sky blue and Chrysophenin be treated with a limited amount of titanous chloride, the yellow is completely destroyed, the blue remaining almost intact. With some colouring matters containing more than one chromophore, the selective action is also noticeable. Thus, on treating Indoine with titanous chloride, the azo-group is destroyed first, and the red colour of the Safranine appears, while with Methylene green, the nitro-group is first attacked, the blue colour of amido Methylene blue making its appearance.

The same reagent may serve for ascertaining whether cotton has been mercerised or not. The white cotton is dyed with Benzopurpurin 4 B, and is then heated with dilute hydrochloric acid, when it instantly turns blue. On gradually adding titanous chloride the dyestuff is destroyed, whether the cotton was mercerised or not, but in the case of mercerised cotton, the colour changes to a pink before the end of the reaction. With ordinary cotton this change is not observed.

In the *Journal of the Society of Dyers and Colourists*, 1901, pp. 61 to 63, Meyenberg gives characteristic reactions of a number of sulphide colours on the fibre.

A. G. Green, \* assisted by H. Yeomann and J. R. Jones, has worked out a scheme for the *Identification of Dyestuffs on Animal Fibres* on the principle, with modifications, of his method for the analysis of colouring matters in substance. The scheme also takes into consideration methods for ascertaining the dyeing properties of the dyestuff on the fibre. Such tests (so-called "stripping tests") are an inversion of the respective dyeing process. With regard to the chemical relationship of the dyestuffs, the modifications consist in using sodium hydrosulphite (in place of zinc dust) for the reduction and potassium persulphate (in place of chromic acid) for the re-oxidation of the colouring matter. The leuco-compounds formed by reduction remain in great part attached to the fibre, whilst the splitting products of the azo-dyestuffs can be entirely removed therefrom by washing.

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

Decolourised by hydrosulphite.			Not altered by hydrosulphite.	Not decolourised, but changed to brown. Original colour restored by air or persulphate.
Colour restored on exposure to air.	Colour not restored by air, but on oxidation with persulphate.	Colour not restored either by air or persulphate.		
Azines, Oxazines, Thiazines, Indigo.	Triphenyl- methane group.	Nitro-, Nitroso-, and Azo- groups.	Pyrons, Acridine, Quinoline, and Thiazol groups. Some members of Anthracene group.	Most dyestuffs of the Anthracene group.

Having ascertained by means of the Tables both the dyeing group 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 limited number of closely related dyestuffs. For distinguishing between these the behaviour with concentrated sulphuric acid or strong hydrochloric acid can be frequently employed. In the appended tables

\* *Journ. Soc. Dyers and Col.*, 1905, p. 236.







TABLE III.—PURPLE AND VIOLET COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.														
Colour is nearly completely stripped - Basic dyestuff. Boil with hydro-sulphite A.			The colour is not stripped.—Acid, Salt, and Mordant dyestuffs. Boil twice for one minute with aqueous ammonia and white cotton.											
Much colour is stripped but cotton remains white.—Acid dyestuff. Boil with hydro-sulphite A.					Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is tinted (salt dyestuff). Boil with sodium acetate and white cotton for two or three minutes.									
Decolourised. The colour returns on exposure to air.	Decolourised. The colour only returns on oxidation with persulphate.	Not altered or only partially decolourised.—Pyrene Group.	Decolourised. The colour does not return on exposure to air, but is restored upon oxidation with persulphate.—Triphenylmethane Group.		Decolourised. The colour returns on exposure to air.—Azine, Oxazine or Thiazine Group.	Decolourised. The colour is not restored either by exposure to air or by oxidation with persulphate.—Azo Group.	The cotton is stained.—Salt dyestuff.	The cotton remains white.—Mordant colour. (Confirm by testing for metallic mordants in ash.) Boil with hydro-sulphite A.						
			The ammoniacal extract is violet or purple.	The ammoniacal extract is colourless, but becomes violet on adding. Spot fibre with conc. HCl.				Colour not altered.—Pyrene Group.	Colour changed to brown.—Alizarin Group. Boil with dilute HCl.	Decolourised. Colour returns on exposure to air.	Decolourised. Colour does not return on exposure to air, but is restored by oxidation with persulphate.	Decolourised. Colour is not restored either by exposure to air or by oxidation with persulphate.		
1.—Basic Violet of also Azine or Oxazine Group.	2.—Basic Violet of methylene Group, Quinacryl Violet.	3.—Fast Acid Violets or Vishnubines.	4.—Acid Violets, Benzoyl Violets, &c.	5.—Alkali Violet.	6.—Red Shades of Soluble Salts.	7.—Lanoxyl or Fast Blue R, &c.	8.—Lanoxyl Violet, Victoria Violet, &c.	9.—Mexican Violet, Lamine Violet, &c.	10.—Gallein.	11.—Alizarin on Fe or Cr.	12.—Alizarin Bordeaux.	13.—Gallinates, Phos. Chromate Blue, &c.	14.—Chrome Violet.	15.—Mordant Azo-Colour.

\* Alizarin on iron becomes brown on boiling with 5 per cent. acetic acid.

TABLE IV.—BLUE COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.																			
Much colour is stripped. Boil with dilute alcohol (1:1) twice for one minute.			Little or no colour is stripped.—Acid, Salt, or Mordant dyestuff. Boil twice for one minute with dilute ammonia (1:100) and small piece of white cotton. Keep the ammoniacal extract.																
Much colour is stripped.—Basic dyestuff. Boil with hydro-sulphite A.			Much colour is stripped but cotton remains white.—Acid dyestuff. Boil with hydro-sulphite A.				Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is tinted (salt dyestuff). Boil with 5 per cent. sodium acetate and white cotton for two or three minutes.												
Decolourised. Original colour returns on exposure to air.—Azine, Oxazine, or Thiazine Group.	Decolourised. A violet colour returns on exposure to air.—Sulphine Azo-Colour.	Decolourised. The colour does not return on exposure to air but is restored by persulphate.—Triphenylmethane Group.	Unfastened. Alizarin or both are present in ash. The blue changed to brick red on spotting with HCl.	Decolourised and colour restored on exposure to air.—Azine, Oxazine, Thiazine, and Indigo Group. Also Prussian Blue.		Decolourised. Colour does not return on exposure to air but is restored by persulphate.—Triphenylmethane Group.	Decolourised. Colour is not restored either by exposure to air or by oxidation with persulphate.—Azo Group.	Not decolourised but changed to black, red.—Alizarin Group.	The cotton is stained. Salt dyestuff. On reduction with hydro-sulphite A the colour is not restored, either by air or persulphate.—Azo Group.	The cotton remains white. Boil with a little sodium oil.									
				Ammon. extract is blue and on adding NaOH becomes violet.	Ammon. extract is colourless. Fe in ash.					Ammon. extract is blue. On boiling with NaOH it becomes violet.	Ammon. extract is colourless but becomes blue on adding.	The solution which on exposure to air or by heating becomes a resinous which solidifies in violet upon heating.	Colour of wool mordanted.—Alizarin Group.	Colour changed to dark brown becoming blue again on exposure to air.—Alizarin Group.	Decolourised. Not entire returns on exposure to air.—Oxazine or Thiazine Group. Treat fibre with conc. H <sub>2</sub> O <sub>2</sub> .	Decolourised. Not entire returns on exposure to air, but is restored by persulphate.—Triphenylmethane Group.	Decolourised. Colour is not restored either by air or persulphate.—Azo Group.		
1.—Methyl red, Blue, and other Blue, &c.	2.—Induline, Janus Blue, Induline, Diamine Blue, &c.	3.—Violet, Blue, Mordant Blue, &c.	4.—Logwood Blue.	5.—Indigo Extract.	6.—Eriochrome.	7.—Prussian Blue.	8.—A. "Wool" Blue.	9.—A. "Patent" Blue.	10.—A. "Soluble" or "Alkali" Blue.	11.—An. Acid Azo-Lanoxyl Blue.	12.—Alizarin, Saphir, Induline, Aniline, Aniline, &c.	13.—Diamine or other Blue, &c.	14.—Indigo.	15.—Alizarin on Fe or Cr.	16.—An. Alizarin Blue (mordant substance).	17.—Soluble Alizarin Blue.	18.—Gallinates, Gallein Blue, &c.	19.—Chrome Blue.	20.—A. Mordant Azo-Blue.

TABLE V.-GREEN COLOURS.

The colour is stripped--Basic dyestuff. Boil with hydro-sulphite A.			The colour is not stripped--Acid, Salt, or Mordant dyestuff. Boil twice for one minute with dilute ammonia (1:100) and a small piece of white cotton.									
Decolourised. A dark violet colour returns on exposure to air--Saffranine-Azo Group.	Decolourised. Original colour returns on exposure to air--Acine, Oxazine, or Thiazine Group.	Decolourised. The colour does not return on exposure to air, but is restored by persulphate--Triphenylmethane Group.	Much colour is stripped but the cotton remains white--Acid dyestuff. Boil with hydro-sulphite A.			Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is stained (salt dyestuff). Boil for two or three minutes with 5 per cent. sodium acetate and a piece of white cotton.			The cotton remains white--Mordant dyestuff. Confirm by testing for metallic mordant in ash. Boil with hydro-sulphite A.			
			Decolourised. Colour returns on exposure to air--Acine, Oxazine, or Thiazine Group.	Decolourised. Colour does not return on exposure to air but is restored by persulphate--Triphenylmethane Group.	Decolourised. Colour is not restored either by air or persulphate--Azo Group.	Colour changes to brown--Alizarin Group.		Decolourised (or changed to light buff).		Colour does not return on exposure to air or upon oxidation with persulphate--Nitroso or Azo Group. Boil with hydro-sulphite acid.	Fibre and solution light brown--Nitroso Group.	Fibre blue and solution colorless--Azo Group.
						Original colour returns on exposure to air.	Original colour does not return on exposure to air, but is restored by persulphate.	Colour returns on exposure to air--Oxazine or Thiazine Group.				
1.--Janus Green or Diamine Green.	2.--Fast Green M, Azine Green, Acine Green, &c.	3.--Malaohite Green, Brilliant Green, Eosin, &c.	4.--Acine Green B.	5.--Acid Greens, Orange Green, Cool Green, &c.	6.--Chrys. Eosins of an Azo, Blue and Yellow.	7.--Diamine Green, Columbin, Chloramine Green, &c.	8.--Cocculin or Green B.	9.--Alizarin Cyanin Green B, Alizarin, Viridin.	10.--Alizarin Green C or B.	11.--Carmine, Black Green, Black Azo Green.	12.--Diamond Green, Chrome Patent Green, &c.	

\* With azo mordant colors the cotton may be slightly tinted, especially if the fixation by chrome is not complete.

TABLE VI.-BROWN COLOURS.

Little or no colour is stripped--Acid, Salt, or Mordant dyestuff. Boil twice for one minute with dilute ammonia.			Little or no colour is stripped--Salt or Mordant dyestuff. Boil for two or three minutes with 5 per cent. sodium acetate and white cotton.			The cotton remains white--Mordant dyestuff. Confirm by testing for metallic mordant in ash. Boil with hydro-sulphite A.			
Much colour is stripped--Basic dyestuff. On boiling with hydro-sulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate--Azo Group.	Much colour is stripped--Acid dyestuff. On boiling with hydro-sulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate--Azo Group.	The cotton is stained--Salt dyestuff. Boil with hydro-sulphite A.	Colour not changed. Boil with dilute hydrochloric acid (1:10).		Decolourised or changed to pale buff or light brown.	Colour returns slowly on exposure to air or quickly on oxidation with persulphate.	Colour not restored either by air or persulphate--Azo Group.	Colour is stripped.	Colour not stripped.
			Colour is stripped.	Colour not stripped.					
1.--Bismarck Brown.	2.--Acid Brown N, Fast Brown O, &c.	3.--Diamine Brown, Eosin Brown, Eosin, &c.	4.--Mikado Brown.	5.--Anthracanthal (Anthracene Brown).	6.--Cutch.	7.--Chromogen.	8.--Anthracene Acid Acid Anthra. Sars Brown, Chrome Brown, Bismarck Brown (See B. Ash).		

TABLE VII.-BLACK AND GREY COLOURS.

The colour is not stripped--Acid, Salt, or Mordant dyestuff. Boil twice for one minute with aqueous alcohol ammonia and small piece of white cotton.			The colour is not stripped--Salt and Mordant dyestuff. Boil with 5 per cent. sodium acetate and small piece of white cotton.			The cotton remains white--Mordant dyestuff. (Confirm by testing ash for mordant). Boil with dilute hydrochloric acid (1:10).				
Much colour is stripped--Basic dyestuff. (N.B. Logwood on Fe mordant also become much paler though solution is not colourless).	Much colour is stripped but the cotton remains white--Acid dyestuff. On boiling with hydro-sulphite A the colour is permanently discharged.	The cotton is stained--Salt and Azo Mordant dyestuff. Permanently decolourised by hydro-sulphite A. Test ash for chrome.	Fibre blue and solution crimson. Test for indigo by boiling with a little outline: blue solution, which on evaporation to dryness gives residue subliming in violet vapour.		Fibre and solution pale brown.	Becomes brown. Original colour slowly returns on exposure to air.	Decolourised. Colour is not restored by exposure to air or persulphate.	Unaffected. Treat fibre with conc. H <sub>2</sub> O <sub>2</sub> .	Colorless solution.	
			Cr is present--Salt dyestuff.	Cr is present--Mordant Azo dyestuff.						Fibre and solution crimson.
1.--Diamine Black, Murex Black, Grey, &c.	2.--Naphthol Black, Black, Valantine Black, &c.	3.--Diamine Black, Black, &c.	4.--Alizarin Black, Chrome Black, &c.	5.--A "Violet Black" (Logwood).	6.--Logwood on Cr.	7.--Logwood on Fe.	8.--Naphthol Black, Alizarin Black B, Blue Black SW.	9.--Diamond Black.	10.--Alizarin Cyanin Black.	11.--Aniline Black.



the subdivision of the groups has been usually omitted as unnecessary, but is given in a few instances (see Table II.), in order to illustrate the general method. For confirmation, the sample should be compared both as to shade and reactions with a dyed pattern of the dyestuff to which it is believed to correspond.

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

*Reagents.*—The following reagents are employed :—

1. Dilute ammonia (1 : 100).
2. Aqueous alcoholic ammonia. 1 c.c. strong ammonia, 50 c.c. strong alcohol, 50 c.c. water.
3. Acetic acid (5 per cent. solution).
4. Dilute alcohol (1 : 1).
5. Dilute hydrochloric acid (1 : 10).
6. Caustic soda. 10 per cent. solution.
7. Hydrosulphite A. 10 per cent. solution of formaldehyde-sodium hydrosulphite.
8. Hydrosulphite B. Hydrosulphite A, with addition of 1 c.c. of glacial acetic acid per 200 c.c.
9. Potassium persulphate. Cold saturated solution.
10. Sodium acetate. 5 per cent. solution.

*Procedure.*—The reactions are performed in test-tubes with pieces of the material about  $\frac{3}{4}$  inch to 1 inch square, which are covered with about 1 inch to  $1\frac{1}{2}$  inches of the reagent. The tests should be carried out exactly as described. In making "stripping tests" the degree of stripping is judged by comparing the depth of shade remaining with that of the original pattern. The colour of the stripping solution is misleading, and can scarcely be relied upon as a guide. 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 also with acid dyestuffs any staining of the cotton by the first strong extract is avoided. In testing with dilute ammonia or sodium acetate, the piece 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 III. and VII.), as in these cases the acid dyestuffs are less easily extracted, and the cotton is more liable to be stained by them. In making reduction tests, the sample is boiled for from one-quarter to one minute with the hydrosulphite, then rinsed well 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, but with others a longer time is required. 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-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) only a light shade may return. Safranine and its azo-derivatives yield on re-oxidation 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.

The reactions given in the annexed analytical tables were mostly ascertained upon the wool fibre, but from a number of tests which were also conducted for comparison upon silk, there is no reason to believe that the latter fibre will exhibit any variations in behaviour. On the other hand,

cotton and other vegetable fibres require rather different treatment, and are described below.

**Mixtures.**—The question of mixtures is not fully dealt with in the paper referred to, but 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 consisting of a mixture of an acid azo-yellow with an acid azo-blue will be distinguishable upon careful reduction with hydrosulphite, since the azo-blue will be reduced first, and the shade will therefore change from green to yellow before it is de-colourised. Neither colour will return on oxidation. Further, if such a compound shade be extracted fractionally with dilute ammonia, the yellow is generally stripped first, and may be transferred to another piece of wool for subsequent tests. Mixtures of colours belonging to different groups will usually exhibit at once their diverse 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 re-oxidation 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 will return upon exposure of the leuco-compound to air, the latter being also restored upon treatment with persulphate. Fractional extraction of the fibre with dilute alcohol or dilute acetic acid can also be employed in many cases to effect a separation or partial separation of the dyestuffs, the extracted colour being then transferred to fresh wool or silk and separately tested.

In a subsequent communication Green\* (in collaboration with Yeoman, Jones, Stephens, and Haley) describes a systematic method for the *Identification of Dyestuffs on Vegetable Fibres*. In many respects the methods employed differ from those used in detecting dyes on wool and silk, principally on account of the influence exerted by mordants on the properties of the dyestuffs, and also on account of 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 affected 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 re-oxidised, this is frequently not the case with cotton.

In order to overcome the difficulty introduced by the presence of a tannin mordant, the latter is removed by boiling with caustic soda; and to prevent this reagent from stripping the dyestuff at the same time, the solution is 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 acid, or preferably with dilute 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, if the colour is appreciably stripped a solution of tannin is added to the acid extract, when a coloured precipitate will result if a basic dyestuff is present.

As already mentioned, many basic dyestuffs fixed upon a tannin mordant

\* *Journ. Soc. Dyers and Col.*, 1907, p. 252.

do not behave normally upon reduction with hydrosulphite, or if the leuco-compound is formed, it may pass into solution and thus render re-oxidation on the fibre impossible. To overcome this difficulty the dyestuff is transferred to wool, and the tests with hydrosulphite and persulphate made on this fibre instead of upon the original cotton.

A class of dyestuffs which occupy a somewhat intermediate position between the basic colours and the mordant colours, since they contain the characteristic groupings of both classes, are the dyestuffs of the Gallocyanine series and the Chrome colours of the Rosaniline series. These products, 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 cannot be transferred to wool by the methods applicable in other cases.

With colours other than basic and acid dyestuffs, the reduction and oxidation tests are performed on the cotton fibre itself, and in order to accelerate the reduction, a small quantity of anthraquinone is added to the hydrosulphite solution. Sulphide colours are identified by the stannous chloride test, carried out in the manner described in the *Journal of the Society of Dyers and Colourists*, 1907, p. 118. Before applying the stannous chloride the fabric is boiled one or two minutes with a 10 per cent. solution of caustic soda. This has the effect of removing free sulphur and most sulphur compounds other than sulphide dyestuffs. It has been found, however, that some "Salt colours" (Direct Cotton Colours) evolve hydrogen sulphide when heated with stannous chloride.

*Reagents.*—The following reagents are used for colours on vegetable fibres:—

1. Dilute ammonia (1 : 100).
2. Caustic soda, 10 per cent. solution.
3. Saline caustic soda, 10 c.c. of 40 per cent. solution caustic soda to 100 c.c. saturated solution of common salt.
4. Formic acid, 90 per cent.
5. Dilute formic acid (1 : 100).
6. Dilute hydrochloric acid (1 : 20).
7. Soap solution, 2 per cent. solution.
8. Tannin solution, 10 grms., with 10 grms. sodium acetate per 100 c.c.
9. Bleaching powder solution, 5° Tw.
10. Hydrosulphite A, 5 per cent. solution of Rongalite or of Hyraldite C extra or of Hydrosulphite N F conc. (formaldehyde-sodium hydrosulphite).
11. Hydrosulphite B. Hydrosulphite A, with addition of 1 c.c. of glacial acetic acid per 200 c.c.
12. Hydrosulphite X. 50 grms. of Rongalite or Hyraldite C extra or Hydrosulphite N F conc. in 125 c.c. of hot water mixed with 1 gm. of anthraquinone ground with a little of the rongalite solution, and the whole heated to 90° C. for one or two minutes, diluted with cold water to 500 c.c., and acidulated with 1.5 c.c. of glacial acetic acid.
13. Potassium persulphate, cold saturated solution (or a 2 per cent. solution of ammonium persulphate).
14. Acid stannous chloride, 10 grms. of stannous chloride, 100 c.c. hydrochloric acid (30 per cent.) and 50 c.c. of water.

*Procedure.*—The reactions are performed in test-tubes, as described for *Animal Fibres* on p. 871. 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 exist 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 table referring to both shades should be employed; since the same general scheme is adopted throughout the tables, this can scarcely give rise to confusion. 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, &c., may be employed.

*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 dilute 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 half a minute with saline caustic soda. It is then well washed to remove all alkali, and is boiled with a piece of white wool (half the size of the cotton or less) in 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 the case of a few dyestuffs which are more difficult to strip (*e.g.*, basic greys) it is necessary to extract the colour with dilute hydrochloric acid (1 : 5), 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.*—A few drops of tannin solution are shaken with the formic acid extract of the colour. 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 also 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.

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 sulphuretted hydrogen and thus may lead to error.

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

The reactions of the various colouring matters on vegetable fibres are given in Tables I. to VII.



# TABLE FIBRE.

## LOURS.

and boil twice with Weak formic acid (1:100)						
the acid extract is not precipitated by Tannin solution. Reduce with hydrosulphite X.						
resulphate :— p). cotton.	The colour is unaffected or changed in shade (becoming yellow, browner, or blue). Apply lead acetate test.					
is not stained. pyridine.	H <sub>2</sub> S is evolved. After reduction with hydro-sulphite the original colour is rapidly restored by air :— Sulphide dyestuff.	No H <sub>2</sub> S is evolved. Boil with soap solution and white mercerised cotton.				
Colour is not stripped. Cr present in ash :— Azo-Mordant Colour.		The white cotton is stained :— Thiazol Salt dyestuff.		The white cotton is not stained :— Mordant or Vat dyestuff.		
		The colour after reduction with hydrosulphite can be diazotised and developed red with beta-naphthol.	The colour after reduction cannot be diazotised and developed.	The reduced colour is yellow or brownish-yellow. Al or Cr in ash.	The reduced colour is brown, restored to orange by persulphate.	The reduced colour is blue, restored to yellow on exposure to air.
te, low R, iamond vazol,	igene, higene, h, Oranges.	veloped : or with Cotton : R, v, Dianil	, Yellow, it Yellow Clayton azol oflavine ulline with e.	as on Al ants.	ge on	











## APPENDIX.

## Systems of Weights and Measures.

*Weights.*—The English standard unit of weight is 1 *pound* avoirdupois containing 7,000 grains.

One pound (lb) = 16 ounces.  
 1 ounce (oz.) = 16 drachms.  
 1 quarter = 28 lbs.  
 1 hundredweight (cwt.) = 4 quarters.  
 1 ton = 20 cwts.

In the metrical system, the gramme (the weight of 1 cubic centimetre of distilled water at 4° C.) is taken as unit for small weights, and the kilogramme (the weight of 1,000 cubic centimetres or 1 litre of water at 4° C.) for greater quantities.

The gramme is divided into 10 decigrammes, 100 centigrammes, or 1,000 milligrammes.

1 gramme = 15·4323 grains.  
 1 kilogramme = 2 204·97 lbs., or  
 10 kilogrammes = 22 lbs., approximately.

The weight of 1 cubic foot of water is 62·424 lbs. (= 1,000 ozs. nearly).

*Measures.*—The English standard unit of length is 1 *yard*, which is subdivided into 3 feet, 36 inches, or 432 lines.

The units used as the measures of surfaces and volumes are the square and cube respectively of the linear units.

Thus—  
 1 square yard = 9 square feet.  
 1 square foot = 144 square inches.

And  
 1 cubic yard = 27 cubic feet.  
 1 cubic foot = 1,728 cubic inches.

The legal measure of capacity is the *Imperial gallon*—that is, a volume holding 70,000 grains or 10 lbs. (avoirdupois) of distilled water at the temperature of 62° F., and under a barometric pressure of 30 inches. The Imperial gallon contains 277·274 cubic inches.

1 gallon = 4 quarts.  
 1 quart = 2 pints.  
 1 pint = 4 gills.

The standard unit of length in the metrical system is the *metre*, which is somewhat longer than the yard.

1 metre = 10 decimetres = 100 centimetres = 1,000 millimetres.  
 1,000 metres = 1 kilometre.  
 1 metre = 1·093633 yards = 3·2809 feet = 39·3708 inches.  
 64 metres = 70 yards, approximately.

The measure of capacity is the *litre*—that is, a volume equal to that of 1 cubic decimetre or 1,000 cubic centimetres.

For small volumes the *cubic centimetre* (generally written c.c.) is taken as unit.

1 litre = 0·220097 gallon = 61·027 cub. in.  
 = 1½ pints, approximately.  
 1 hectolitre (100 litres) = 22 gallons, approximately.

\* The English measures of weight, length, and capacity are also used in the United States, with the exceptions, however, that the legal measure of capacity is the apothecary's or wine gallon, and that a short ton = 2,000 lbs. is very generally employed, the English ton = 20 cwts. being called a gross ton. 1 wine gallon = 231 cubic inches = 3·785 litres.

### Specific Gravities.

By *specific gravity* or *density* is meant the weight of a solid or liquid compared with the weight of an equal volume of water at 4° C. By the metrical system, the weight of one cubic centimetre of the substance in grammes gives at once its specific gravity.

The specific gravity of solid bodies may be determined by weighing a piece of the substance, first in the air, and then in distilled water; the difference in weight will indicate the weight of water displaced, and the specific gravity can be thus calculated. Or, the weight of a known volume of the substance is determined in the specific gravity bottle.

Of much greater importance to the dyer is the determination of the specific gravity of liquids or solutions, for the purpose of determining their degree of purity or of obtaining a rough estimate of the amount of substance dissolved. The most exact results are arrived at by means of the specific gravity bottle—a small glass bottle or flask, generally of 25 or 50 c.c. capacity, provided with a stopper, through which a fine hole is pierced. The flask is filled with the liquid or solution under examination, the stopper inserted, and the superfluous liquid which escapes through the hole in its centre is wiped off. The flask containing the solution is now weighed, a counterweight exactly equal to that of the empty flask being placed on the opposite pan of the balance. If the flask is one of 25 c.c. capacity, the weight in grammes thus obtained will give at once the weight of 25 c.c. of the solution, and dividing this by 25, will give the specific gravity. If, for instance, the weight of the liquid were found to be equal to 30 grammes, the specific gravity of the liquid would be  $\frac{30}{25} = 1.20$ . In case no other apparatus is at hand, a determination may be made by measuring 10 c.c. of the liquid from a pipette, and weighing it in a tared flask or weighing bottle. In order now to ascertain the amount of substance in solution, it is necessary to refer to tables which have been worked out for most of the substances used in dyeing, with the exception of the dyes themselves. Thus, if the solution under examination had been one of sulphuric acid, and showed a density of 1.11, we should refer to the table on p. 164, and see at a glance that the solution contained 16 per cent. of sulphuric acid ( $H_2SO_4$ ). Or, if it were one of stannic chloride, we should refer to the table of stannic chloride on p. 274, and see that it contained 18 per cent. of stannic chloride ( $SnCl_4 + 5 H_2O$ ), and so on.

It should be borne in mind that in estimating the strength of solutions by determining their specific gravities, the results will be of no value whatever if more than one substance be in the solution. Thus the specific gravity of a solution of nitrate of iron, containing an admixture of Glaubersalt, is valueless, since it does not tell us to what extent the increase in the density of the liquid is due to the nitrate of iron or the sodium sulphate.

In determining specific gravities, it should also be remembered that temperature materially affects the correctness of the results. Most of the tables are constructed for 15° C. or 60° F., and the determinations should consequently be done as nearly as possible at this temperature. The following may serve as an instructive example of the effect of temperature on the density:—If a small quantity of aniline oil is poured into a test-tube containing pure water, it will sink at the ordinary temperature, the oil being then slightly heavier than water. But the coefficient of expansion of aniline oil is greater than that of water, and, on heating the contents of the tube, the oil slowly rises, and ultimately floats on the surface, having now a less specific gravity than water.

*Hydrometers.*—The specific gravity bottle is not often employed in dye-houses, its place being taken in the works by the more convenient hydrometers. The hydrometer most in use consists of a glass tube (the stem), with a large and a small bulb at the end. The large bulb is filled with air to give the instrument buoyancy, while the smaller bulb at the bottom serves for the reception of shot or mercury, which causes it to stand vertically in a liquid. For liquids heavier than water, the size of the larger bulb and the quantity of mercury are so regulated as to cause the stem to sink within about half an inch of the top in distilled water at 60° F. This point is marked 1.000. By immersing the instruments in liquids of known specific gravity, and noting each time the point to which the stem rises out of the liquid, the other values are obtained, which are transferred to a scale inside the stem. For liquids lighter than water, the point marked 1.000 is made to show at the bottom of the stem; the graduation is done as before.

On the scale of the specific gravity hydrometer, the differences corresponding to equal increases in density are not equal, so that an accurate graduation of the tube shows unequal intervals.

By means of such hydrometers the specific gravity of a liquid can be determined by simply immersing the instrument in the liquid contained in a glass cylinder, and reading off the specific gravity at the point to which the stem sinks into the liquid. Care should, of course, be taken that the instrument does not touch the side of the vessel.

Hydrometers graduated in degrees, such as those of Twaddle, Baumé, Beck, Cartier, are in much more general use than the specific gravity hydrometer.

The degrees in *Twaddle's* hydrometer, which is in general use in England, bear a direct relationship to the specific gravity. The degree Twaddle is obtained from the specific



gravity by the following rule:—Multiply by 1000, subtract 1000, and divide by 5. Thus, in order to convert the specific gravity 1.205 into degrees Twaddle, we have—

$$1.205 \times 1000 = 1205$$

$$\begin{array}{r} 1000 \\ 5 \overline{) 205} \\ \hline 41 \end{array}$$

41° Tw.

To convert degrees Twaddle into specific gravity: Multiply by 5, add 1000, and divide by 1000. Thus for 32° Tw. we should have the following:—

$$32 \times 5 = 160$$

$$\begin{array}{r} 1000 \\ 1000 \overline{) 1160} \\ \hline 1.160 \end{array}$$

1.160 spec. gravity.

On the Continent and in the United States, Baumé's hydrometer is in general use. For liquids lighter than water the specific gravity values, and not degrees are used in England.

COMPARATIVE TABLE OF HYDROMETER DEGREES BAUMÉ AND TWADDLE.

B.	Tw.	B.	Tw.	B.	Tw.	B.	Tw.
1	1.4	18	28.4	35	64.0	52	112.6
2	2.8	19	30.4	36	66.4	53	116.0
3	4.4	20	32.4	37	69.0	54	119.4
4	5.8	21	34.2	38	71.4	55	123.0
5	7.4	22	36.0	39	74.0	56	127.0
6	9.0	23	38.0	40	76.6	57	130.4
7	10.2	24	40.0	41	79.4	58	134.4
8	12.0	25	42.0	42	82.0	59	138.2
9	13.4	26	44.0	43	84.8	60	142.0
10	15.0	27	46.2	44	87.6	61	146.4
11	16.6	28	48.2	45	90.6	62	150.6
12	18.2	29	50.4	46	93.6	63	155.0
13	20.0	30	52.6	47	96.6	64	159.0
14	21.6	31	54.8	48	99.6	65	164.0
15	23.2	32	57.0	49	103.0	66	168.4
16	25.0	33	59.4	50	106.0	67	173.9
17	26.8	34	61.6	51	109.2	68	..

Thermometers and Thermometric Scales.

Thermometers serve for indicating the degree of temperature, and they are useful, if not indispensable, to the dyer in carrying out many operations of washing, mordanting, dyeing, ageing, and drying. The thermometer most in use is the ordinary mercurial thermometer. Three scales are in use—namely, those of Fahrenheit, Réaumur, and Celsius (the Centigrade scale). Of these the Fahrenheit scale is used principally in this country and in the United States, the Réaumur scale in Germany and Austria, while the Celsius or Centigrade scale, used in France and Scandinavia, although used principally for scientific purposes, is gradually taking the place of the two older scales.

In the graduating of a thermometer, two points are taken as standards—viz., the freezing point and the boiling point of water at a pressure equal to that of 760 mm. of mercury. For the different scales these are fixed at the following points:—

	Freezing Point.	Boiling Point.
Fahrenheit,	32°	212°
Réaumur,	0°	80°
Centigrade,	0°	100°

Therefore, 180° F. = 80° R. = 100° C.

To convert the degrees in one scale into those of another we have the simple formulæ:—

C. to R.	°R. = $\frac{4}{5}$ °C.	F. to C.	°C. = $\frac{5}{9}$ (°F. - 32).
R. to C.	°C. = $\frac{5}{4}$ °R.	R. to F.	°F. = $\frac{9}{5}$ °R. + 32.
C. to F.	°F. = $\frac{9}{5}$ °C. + 32.	F. to R.	°R. = $\frac{5}{9}$ (°F. - 32).

TABLE FOR CONVERTING DEGREES CENTIGRADE (CELSIUS) INTO DEGREES FAHRENHEIT.

Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.
32	0·00	102	38·88	172	77·77
34	1·11	104	40·00	174	78·88
36	2·22	106	41·11	176	80·00
38	3·33	108	42·22	178	81·11
40	4·44	110	43·33	180	82·22
42	5·55	112	44·44	182	83·33
44	6·66	114	45·55	184	84·44
46	7·77	116	46·66	186	85·55
48	8·88	118	47·77	188	86·66
50	10·00	120	48·88	190	87·77
52	11·11	122	50·00	192	88·88
54	12·22	124	51·11	194	90·00
56	13·33	126	52·22	196	91·11
58	14·44	128	53·33	198	92·22
60	15·55	130	54·44	200	93·33
62	16·66	132	55·55	202	94·44
64	17·77	134	56·66	204	95·55
66	18·88	136	57·77	206	96·66
68	20·00	138	58·88	208	97·77
70	21·11	140	60·00	210	98·88
72	22·22	142	61·11	212	100·00
74	23·33	144	62·22	214	101·11
76	24·44	146	63·33	216	102·22
78	25·55	148	64·44	218	103·33
80	26·66	150	65·55	220	104·44
82	27·77	152	66·66	222	105·55
84	28·88	154	67·77	224	106·66
86	30·00	156	68·88	226	107·77
88	31·11	158	70·00	228	108·88
90	32·22	160	71·11	230	110·00
92	33·33	162	72·22	232	111·11
94	34·44	164	73·33	234	112·22
96	35·55	166	74·44	236	113·33
98	36·66	168	75·55	238	114·44
100	37·77	170	76·66	240	115·55

### Evaporation and Boiling.

*Evaporation.*—When water is exposed to the air it evaporates—that is, its particles pass into the surrounding atmosphere in the form of vapour. The rate of evaporation will depend upon the amount of moisture present in the air, the barometric pressure, the velocity of the air, and the temperature. In a perfectly dry atmosphere, or in a vacuum, the following figures show the effect of temperature in this respect:—

TABLE SHOWING THE BAROMETRIC PRESSURE OF SATURATED AQUEOUS VAPOUR IN MILLIMETRES FOR A GIVEN TEMPERATURE.

Degrees C.	Millimetres.	Degrees C.	Millimetres.
-10	2·09	50	91·98
0	4·6	55	117·48
+ 5	6·53	60	148·79
10	9·16	65	186·94
15	12·70	70	233·08
20	17·60	75	288·50
25	23·55	80	354·62
30	31·55	85	433·00
35	41·83	90	525·40
40	54·91	95	633·69
45	71·39	100	760·00

In a perfectly dry current of air the rate of evaporation in drying, for instance, would be proportional to these figures.

**Boiling.**—As will be seen from the foregoing table, the tension of aqueous vapour becomes at 100° C. equal to that of the pressure of the atmosphere (at or near the sea level). Water is then said to boil—that is, if it is exposed to the air at the ordinary barometric pressure. But if confined in closed vessels (a boiler, for instance) the following relations between pressure and temperature are observed :—

Degrees C.	Pressure.	Degrees C.	Pressure.
100	1 atmosphere.	159°22	6 atmospheres.
120°60	2 "	165°34	7 "
133°91	3 "	170°81	8 "
144°00	4 "	175°77	9 "
152°22	5 "	180°31	10 "

Dissolved substances materially affect the boiling point of water. Thus, a saturated salt solution only boils at 109° C. In experimental dyeing, soluble salts (e.g. calcium chloride) are sometimes added to the heating bath for the purpose of raising the temperature sufficiently to cause the water in the dye-pots to boil.

The boiling point of water is also affected by the pressure of the atmosphere. The greater the height above the sea-level at which the works are situated, the lower will be the boiling point of the water. Ordinarily, the difference is very small, and has no material influence; but under certain conditions it might materially affect certain dyeing operations. By exhausting the air from a vessel containing water, the liquid may be made to boil at the ordinary temperature.

In transforming water into vapour or steam, a large amount of energy (in the form of heat) has to be expended. In physics the amount of heat is measured by heat units or calories, one calorie being the amount of heat necessary to raise a unit (1 gramme) of water through 1° C. Thus, in order to raise 1 gramme of water from 0° to 100° C., 100 calories would be required. The same amount of heat would suffice on the other hand to raise 100 grammes of water from 0° to 1°, or 5° to 6°, or 25 grammes of water from 0° to 4°, and so on. But in order to raise 1 gramme of water at 100° into steam of the same temperature, the amount of heat required is no less than 537 calories. In the operation of drying, or in the use of open dye-vessels or non-condensing engines, the quantity of so-called *latent heat* which thus passes away into the surrounding atmosphere is absolutely lost for all practical purposes. In like manner a great loss of heat may be sustained by condensation in steam-pipes which are badly or insufficiently insulated.

The heat apparently lost in the conversion of water into steam shows itself again in the condensation of the steam into water, 1 gramme of steam at 100° containing sufficient heat to raise 537 grammes of water 1° C. Thus, in the heating of dye-vats by steam practically no heat need be lost if the pipes are well insulated, the steam merely serving as a convenient medium for transferring the heat produced in the boiler to the part of the works in which it is required.

With a good boiler installation, 1 lb. of coal should convert not less than 7 lbs. of water into steam at 100°, and this might be practically taken as equivalent to  $7 \times 537 = 3,759$  pound-calories. From this it would, for example, be easy to calculate the amount of coal necessary to raise a 300-gallon vat of water from the ordinary temperature (say 10° in winter) to boiling point. Using the pound as unit in the calories, we have 300 gallons or 3,000 lbs. to be raised from 10° to 100°, or through 90° C. =  $3,000 \times 90$ , or 270,000 pound-calories.

Now 3,759 pound-calories require 1 lb. coal.

Or 1 " "  $\frac{1}{3759}$  "

And 270,000 pound-calories require  $270,000 \times \frac{1}{3759} = 72$  lbs. about.

And taking the coal at 10s. per ton, this would represent about 4d. in coal.

A calculation of this kind can only give a rough estimate, no account being taken of possible condensation in the pipes, but it is practically independent of the pressure in the boiler.

### Hygroscopy.

**Moisture in the Air.**—When water evaporates it is taken up or dissolved by the surrounding atmosphere. The amount of water capable of being thus absorbed varies directly with the pressure and the temperature of the air. When the evaporation has proceeded for a certain time in a closed space the air becomes incapable of absorbing any further quantities of water, and is then said to be saturated.

In the operation of "ageing," it is frequently necessary to ascertain the relative moisture in the chamber. This is generally effected by means of the wet- and dry-bulb thermometers, the latter being an ordinary thermometer, while the bulb of the former is kept moist by being enveloped in wet muslin or calico. The drier the air the more rapidly will the water round the wet-bulb thermometer evaporate. In evaporating, the water absorbs heat from its immediate surroundings, and the temperature consequently falls in proportion to the dryness of the air. In an atmosphere saturated with moisture, the two thermometers will show the same degree of temperature. The amount of moisture actually present in the air can be obtained by reference to tables. This, however, is seldom done in the works, the difference in the temperatures of the two thermometers being a sufficient guide to work by.

Another instrument for measuring the moisture in the atmosphere is the hair-hygrometer, the action of which depends upon the fact that a hair will expand in a moist atmosphere, and contract in a dry one. Of the various instruments constructed on this principle, that of Saussure, as improved by Hottinger (see Fig. 121), deserves attention.

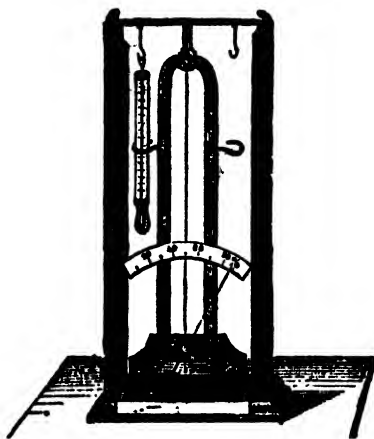


Fig. 121.—Hottinger's hair-hygrometer.

It contains a well cleansed hair, made fast at its upper end, while the lower end passes round a small pulley, to which is attached a finger. The hair is kept stretched by means of a weight of half a gramme attached to its lower extremity. When drying, the hair contracts, and draws the finger to the left; when moistened it expands, and the weight draws the finger to the right. The instrument is enclosed in a small glass case when not in use. Before being used it is tested by simply inserting a sliding frame of wetted muslin into the case. The air will quickly become saturated with moisture, and the corresponding temperature is read off in the thermometer. The index of the hygrometer should now rise to 100; if this is not the case it is brought to that point by turning the index or finger. After withdrawing the wet muslin, the hygrometer is exposed to the atmosphere, the moisture of which is to be determined. The point on the scale at which the index remains stationary indicates directly the percentage of saturation of the air by moisture.

When air saturated with moisture is cooled, the moisture condenses and becomes visible as fog or mist. This is especially the case on a cold day in dye-houses where many open dye-vats are being used. Under such conditions the whole room is frequently filled with such a dense fog that the work may become impeded. The admission of cold air from the outside only makes matters worse, causing more condensation. By heating the air before it enters the room, the fog or "steam" could be done away with to a great extent or altogether. The evil is also greatly lessened by fixing a wooden hood, connected with a fan, directly over each dye-vat, so that the steam is drawn off before it has time to get into the air of the room.

### Light and Colour.

According to the present accepted theory, light is produced by the rapid undulatory or wave movements of the universal ether. These movements take place in any direction perpendicular to the path of the ray in ordinary light, whereas in so-called polarised light the ether oscillates in one plane only. The wave-lengths as well as the number of oscilla-

tions per second vary with different kinds of light, as is seen from the following measurements of Fresnel :—

COLOUR OF LIGHT.	Wave-lengths in air, expressed in millimetres.	Number of oscillations per second (in billions).
Violet, . . . . .	0·000423	735
Dark blue, . . . . .	0·000449	691
Light blue, . . . . .	0·000475	653
Green, . . . . .	0·000511	607
Yellow, . . . . .	0·000551	563
Orange, . . . . .	0·000583	532
Red, . . . . .	0·000645	500

When a ray of light passes from one transparent medium into another of different density, its path is altered, and the light is said to be *refracted*. The degree of refraction varies with the difference in the density of the two media and with the wave-length, those rays being refracted most which have the smallest wave-length. Thus, by passing a ray of white light through a glass prism, we are able to decompose it into its constituent parts; in other words, to analyse it. White sunlight decomposed in this manner yields a so-called *spectrum*, in which the eye is able to detect the following colours—red, orange, yellow, green, blue, and violet. The coloured light in 1,000 parts of white sunlight is distributed, according to Rood, as follows :—

Red, . . . . .	54	Yellowish-green, . . . . .	121
Orange-red, . . . . .	140	Green and blue-green, . . . . .	134
Orange, . . . . .	80	Sky-blue, . . . . .	32
Orange-yellow, . . . . .	114	Blue, . . . . .	40
Yellow, . . . . .	54	Ultramarine and blue-violet, . . . . .	20
Greenish-yellow, . . . . .	206	Violet, . . . . .	5

The solar spectrum contains besides, other rays beyond the violet (ultra-violet rays) and beyond the red (ultra-red or heat rays), which are not visible to the eye.

Each colour in the spectrum consists of uniform or homogeneous light; it cannot be further decomposed. But the colours which we perceive in everyday life never consist of homogeneous light; they are always mixtures of differently coloured rays. This fact can be readily demonstrated by means of the *absorption-spectrum*, produced by passing a ray of white light through a solution of the colour, and observing the result in the spectroscope, or by the direct analysis of the light reflected from the object in the same instrument. Thus, a solution of picric acid in water, and a piece of flannel dyed with this colouring matter, both produce in our eye the impression of an intense yellow. But when we come to analyse the yellow in the manner indicated, we shall find that it not only contains the yellow of the spectrum, but also all the rays from the red end as far as the blue and violet, which latter are extinguished. The light entering our eye contains indeed all the yellow of the spectrum, but in addition to this it contains the red, green, and bluish-green parts of the spectrum. But these are balanced in such proportions as to produce white, and our impression of yellow is caused, therefore, by the pure yellow of the spectrum mixed with a large proportion of white light. Similarly, a solution of Magenta does not appear red because it allows only the red rays of the spectrum to pass, but because it absorbs that portion of the spectrum which is *complementary* to it—viz., the green—allowing all the rest to pass, and our impression of red is, therefore, produced by the red of the spectrum mixed with a large proportion of white. Again, a solution of indigo extract gives an absorption-spectrum which shows a dark band in the yellow. It allows the blue and all the other rays to pass, except yellow, with the result that a blue mixed with a large proportion of white is produced. Other colouring matters behave in a similar manner; no colour is known which allows only homogeneous light to pass. To the presence of white light in a colour is due in a great measure its brilliancy.\* Each dyestuff has its own characteristic absorption-spectrum, and on this will depend to a very great extent its behaviour in admixture with other colours and its appearance under different illuminations.† To the absorption-spectra are

\* See A. Scheurer, "On yellow and the limit of the yellow sensation," *Journ. Soc. Dyers and Col.*, p. 195, 1891.

† For a full account of the absorption spectra of the artificial dyestuffs, the reader is referred to Dr. J. Formánek's work, *Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege*. Julius Springer, Berlin.

also due the effects produced by mixing two or more colouring matters. Thus picric acid and indigo extract yield green, but the effect of green is not produced by the one only allowing yellow rays, the other only blue rays to pass, but because both allow the green rays to pass through unchanged, accompanied by a certain amount of white light.

It has already been seen that white solar light can be decomposed into a number of coloured lights. By reuniting these, white light is again produced. The same effect—viz., white—is also produced by mixing two lights, the colours of which are complementary to each other—for instance, orange and indigo, red and green. Exactly the opposite is the case with solutions of two complementary colours. Thus a solution of two such complementary colours as indigo-blue and orange, if sufficiently concentrated, allows no light to pass through, and a black results. If the solution be diluted far enough greys will result—i.e., mixtures of black and white.

The behaviour of dyed textile fibres is analogous to that of the solutions of the corresponding dyestuffs. The fibres are all translucent, and hold the colours or rather their lakes in a state of solid solution. The light which strikes a piece of dyed material penetrates to a certain distance into the substance of the fibre, is deprived of some of its constituents, and is reflected back, entering the eye with the same result as would have been obtained by passing it through a solution of the dyestuff or dyestuffs employed.

The three simple or primary colours at present adopted by physicists are red, green, and blue. But for several reasons it is better for the dyer to accept as his primary colours the older classification of red, yellow, and blue. Add to these black and white, and we have all the primary impressions which the eye is capable of receiving. From red and yellow we obtain orange, from yellow and blue, green, and from blue and red, violet. Red, yellow, and blue mixed together in the right proportion give black or grey, as in the case with the complementary colours.

F. V. Kallab's colour analyser (Engl. Pat., No. 15,263, 1907) represents a convenient device for indicating how any given colour may be matched. It consists essentially of three superposed discs of transparent celluloid which can be turned round a common axis. The bottom one is red, the second yellow, and the third blue. The discs are not uniformly coloured throughout, but are built up of eight sectors representing the colour (*e.g.*, red) from the darkest to the palest shade. One of the sectors is colourless. A fourth disc, made up of different shades of grey, is provided with the instrument and is found necessary in the matching of certain colours.

The colour of an object will depend to a very great extent on the nature of the light with which it is illuminated. This is a matter of fact which few can have failed to observe in everyday life. Even during the day-time there is a marked contrast between the green colour of the leaves of trees and of meadows in the morning and evening, which is not due to a change in the green, but to a change in the light. Still more marked is the contrast shown by many colours in bright daylight and in gas or lamp light. Most yellow, green, blue, and certain compound shades are very difficult to judge by gaslight. Some colours appear totally different by gas or lamp light to what they do by daylight. One of the most striking examples of this kind is the green produced by a mixture of Acid violet 7 B and Naphthol-yellow S. By daylight it is a full, but not very brilliant, green, whereas by gas or lamp light it is not possible to detect in it the slightest trace of green; it is simply a dull violet. In the dyeing of compound shades, due notice should be taken of this and similar facts. One can easily imagine, for instance, the result in a yarn-dyed figured dress-fabric, if two lots of the yarn had been dyed the same colour but with different dyestuffs by different dyers, and used by the manufacturer indiscriminately either in the warp or weft. The pieces would probably look all right in the day-time, but at night the effect might be grotesque.

The best light for the matching of colours during the day-time is that coming from the north because it is least subject to variations.

When dyers were limited to a small range of colouring matters—*e.g.*, when the only blue was Indigo—there was not so much trouble in colour matching, but the multiplicity of artificial dyes, each with its own peculiarities, has greatly increased the difficulties of the dyer in this direction. Two blues, for example, may match in daylight, but in gaslight one may appear greener, the other redder.

For these various reasons the need of an artificial light which can be relied upon for colour matching has long been felt, not only by dyers but also by calico and paper printers, &c. It is well known that none of the ordinary artificial lights are at all reliable as regards colour matching. The electric arc light is more satisfactory than the incandescent electric or gas light, and has been largely used in dye-houses. The light produced by burning magnesium wire or ribbon has also been much employed in matching, but this also differs considerably from standard daylight. The light reflected from a white cloud during the bright hours of the day may be taken as a standard white light, and all other illuminants will be defective to the extent to which their spectra depart from that of this standard.

In ordinary gaslight and incandescent electric light there is present a large excess of rays from the red end of the spectrum, and a deficiency of rays from the violet end. Incandescent gaslight, electric arc light, and the magnesium light approach more nearly to the standard, but these contain an excess of violet as well as of red rays.

It should be pointed out that a light may be perfectly colourless, and, therefore, may appear exactly like standard white light, and yet be absolutely useless for colour matching because certain spectral rays are entirely absent. Any pair of complementary coloured lights, such, for example, as suitable red and green, will give such a white light, but a violet or blue viewed in light of this character might appear quite black. To be of value in colour matching a light must, therefore, contain all the spectral hues in the same proportion as in standard white light, and the problem of correcting any given illuminant is that of reducing its spectrum to that of daylight.

It is well known that there is much greater risk attending the matching of certain colours than is found with others. Reds, for example, often present little difficulty, and may be matched by almost any sufficiently powerful light, but blues are very uncertain, while greens, browns, drabs, olives, and blacks give much more serious trouble. The reason for this becomes apparent on making a careful spectroscopic examination of such hues. A full shade of a typical red is transparent to red light only, and all illuminating agents contain a sufficiency of red. Blue dyes, on the other hand, transmit not only blue light but violet and green, and usually are also more or less transparent to red light. An excess of red rays in the light used for matching thus gives undue prominence to the red in the blue, which is further greatly accentuated if the illuminating agent is deficient in violet.

It has been found that colours transmitting rays from two widely separated portions of a spectrum are peculiarly susceptible to change in different illuminating agents.

The most reliable artificial light for use in colour matching is the "Dalite" lamp, the joint invention of Mr. Arthur Dutton and Professor W. M. Gardner, of the Technical College, Bradford. In this the source of light is an electric arc of the enclosed type. The light from an arc lamp consists partly of the rays emitted from the glowing carbons and partly from the arc itself, the mixture of the two giving a light with an excess of rays at both the red and violet ends of the spectrum. In the Dalite lamp these excess rays are cut off by absorption in a special glass coloured with cupric silicate, the rays being previously thoroughly mixed by passing through suitable media. A steady uniform white light is thus produced which shows colours in their true daylight aspect, and which is sometimes even more reliable for colour matching than daylight itself. Many modern dye-houses are now equipped with these lamps, and the difficulties hitherto experienced in matching have thus been overcome, matching having been thereby rendered possible at any hour of the day or night.

For fuller details on the subject of Light and Colour, the reader may refer to the following works:—Chevreul on *Colour*; Rood's *Modern Chromatics*; Church's *Colour* (Cassell & Co.).

TABLE OF ELEMENTS, THEIR SYMBOLS AND ATOMIC WEIGHTS (O = 16).

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
1. Aluminium, . . .	Al	27·10	42. Neodymium, . . .	Nd	144·30
2. Antimony, . . .	Sb	120·20	43. Neon, . . .	Ne	20·00
3. Argon, . . .	Ar	39·90	44. Nickel, . . .	Ni	58·68
4. Arsenic, . . .	As	74·96	45. Niobium, . . .	Nb	93·50
5. Barium, . . .	Ba	137·37	46. Nitrogen, . . .	N	14·01
6. Beryllium, . . .	Be	9·10	47. Osmium, . . .	Os	190·90
7. Bismuth, . . .	Bi	208·00	48. Oxygen, . . .	O	16·00
8. Boron, . . .	B	11·00	49. Palladium, . . .	Pd	106·70
9. Bromine, . . .	Br	79·92	50. Phosphorus, . . .	P	31·00
10. Cadmium, . . .	Cd	112·40	51. Platinum, . . .	Pt	195·00
11. Cæsium, . . .	Cs	132·81	52. Potassium, . . .	K	39·10
12. Calcium, . . .	Ca	40·09	53. Praseodymium, . . .	Pr	140·60
13. Carbon, . . .	C	12·00	54. Radium, . . .	Ra	226·40
14. Cerium, . . .	Ce	140·25	55. Rhodium, . . .	Rh	102·90
15. Chlorine, . . .	Cl	35·46	56. Rubidium, . . .	Rb	85·45
16. Chromium, . . .	Cr	52·00	57. Ruthenium, . . .	Ru	101·70
17. Cobalt, . . .	Co	58·97	58. Samarium, . . .	Sm	150·40
18. Copper, . . .	Cu	63·57	59. Scandium, . . .	Sc	44·10
19. Dysprosium, . . .	Dy	162·50	60. Selenium, . . .	Se	79·20
20. Erbium, . . .	Er	167·40	61. Silicon, . . .	Si	28·30
21. Europium, . . .	Eu	162·00	62. Silver, . . .	Ag	107·88
22. Fluorine, . . .	Fl	19·00	63. Sodium, . . .	Na	23·00
23. Gallium, . . .	Ga	69·90	64. Strontium, . . .	Sr	87·62
24. Gadolinium, . . .	Gd	157·30	65. Sulphur, . . .	S	32·07
25. Germanium, . . .	Ge	72·50	66. Tantalum, . . .	Ta	181·00
26. Gold, . . .	Au	197·20	67. Tellurium, . . .	Te	127·50
27. Helium, . . .	He	4·00	68. Terbium, . . .	Tb	159·20
28. Hydrogen, . . .	H	1·008	69. Thallium, . . .	Tl	204·00
29. Indium, . . .	In	114·80	70. Thorium, . . .	Th	232·42
30. Iodine, . . .	I	126·92	71. Thulium, . . .	Tu	168·50
31. Iridium, . . .	Ir	193·10	72. Tin, . . .	Sn	119·00
32. Iron, . . .	Fe	55·85	73. Titanium, . . .	Ti	48·10
33. Krypton, . . .	Kr	83·00	74. Tungsten, . . .	W	184·00
34. Lanthanum, . . .	La	139·00	75. Uranium, . . .	U	238·50
35. Lead, . . .	Pb	207·10	76. Vanadium, . . .	V	51·20
36. Lithium, . . .	Li	7·00	77. Xenon, . . .	X	130·7
37. Lutetium, . . .	Lu	174·00	78. Ytterbium, . . .	Yb	172·00
38. Magnesium, . . .	Mg	24·32	79. Yttrium, . . .	Y	89·00
39. Manganese, . . .	Mn	54·93	80. Zinc, . . .	Zn	65·37
40. Mercury, . . .	Hg	200·00	81. Zirconium, . . .	Zr	90·60
41. Molybdenum, . . .	Mo	96·00			



## INDEX.

Pages 749-874 refer to the Analytical Part.

ABBREVIATIONS of Part VII., 374.

- Absolute alcohol, 298.  
 Acacia catechu, 368.  
 Acetates, 170, 764.  
 Acetic acid, 170, 763.  
 Acetin, 300.  
 — blue, 490.  
 Acetinduline, 490.  
 Acetopurpurin, 393.  
 Acetylene blue, — sky-blue, 422.  
 Acid alizarin black, 636; — blue, 611;  
 — green, 612; — grey, 612.  
 — alizarin colours, 634.  
 — anthracene colours, 634.  
 — azo rubin, 528; — azo yellow, 519.  
 — black, 563; — blue, 549; — brown,  
 556; — crimson, 528; — fuchsine, 533;  
 — green, 553; — magenta, 533, 534;  
 — mauve, 541; — rhodamine, 534; — ros-  
 amine, 541; — rubin, 533; — violet, 537,  
 538, 539, 541; — yellow, 516, 518, 519.  
 — chrome colours, 631, 634.  
 — colours, 509 (Single brands, see also  
 above, *Acid azo rubin*, *Acid black*, &c.).  
 — Application of, 510.  
 — Behaviour of, towards reducing  
 agents, 510.  
 — Constitution of, 509.  
 — Experimental dyeing with, 741.  
 — Method of dissolving, 511.  
 — Methods of removing, from the fibre,  
 515.  
 Acidimetry, 751.  
 Acids, 163.  
 — Action of, on cotton, 28, 31.  
 — on silk, 63.  
 — on wool, 54.  
 Acridine golden yellow, 473; — orange, 473;  
 — red, 469.  
 Acrolein, 174.  
 Adjective colours, 2.  
 Adrianople red, 579.  
 Afghan yellow, 407.  
 After-chroming methods, 384, 631.  
 Ageing, 7, 235, 207, 649.  
 — of logwood, 331.  
 Akme-yellow, 520.  
 Alcohol, Absolute (Ethyl or Ordinary), 311.  
 — Amyl, 300.  
 — Methyl, 298.  
 Aldehyde, 299.  
 Algal colours, 672.  
 Alizadine black, 632.  
 Alizarin, 362, 570, 573.  
 — Application of, 579.  
 — to cotton with alumina mordants,  
 579.  
 — to cotton with mordants other than  
 alumina, 597.  
 — to linen, 598.  
 — to silk, 600.  
 — to wool, 598.  
 — blue shade, yellow shade, for red, for  
 violet, G, V, 578.  
 — Commercial, 578 (see also 362).  
 — Constitution of, 571.  
 — lakes, 573; — pinks, 596.  
 — No. 6, 602.  
 — powder, S, 2S, 3S, W, WS, 3WS, 577,  
 601.  
 — Reactions of, 578.  
 — red, syn. of *Alizarin*.  
 — red dyeing processes, 594.  
 — azo colours, 634.  
 — astrol, 613; — black, 611, 625; — blue,  
 607; blue S, 609; blue-black, 615;  
 — bordeaux, 603; — brown, 602; — car-  
 mine, 601; Commercial, 578 (see also 362);  
 — cardinal, 606; — cyanin, 604, 605;  
 — cyanin green, 614; — cyclamin, 605;  
 — dark blue, 610; — dark green, 627;  
 — emeraldol, 613; — fast grey, 615; — gar-  
 net, 606; — green S, 610, 611; — green B,  
 G, 627; — green, see also *Coerulein*; — helio-  
 trope, 615; — indigo blue S, 610; — irisol,  
 613; — maroon, 606; — orange, 607;  
 — powder, 577, 601; — red, syn. of *Alizarin*;  
 — rubinol, 614; — saphirol, 612; — sky-  
 blue, 613; — violet, 597, 616; — viridine,  
 614; — yellow A, C, 623; — yellow F S,  
 644; — yellow G G, R, 642.  
 — colours, 564, 571 (Single brands, see also  
 above, *Alizarin*, and *Alizarin astrol*, &c.).  
 — General methods of dyeing, 564.

- Alkali (*Solway soda*), 200.  
 — Action of, on cotton, 32.  
 — on silk, 64.  
 — on wool, 51, 55.  
 — blue, 544; — brown, 435; — dark brown, 436; — fast green, 554; — garnet, 394; — orange, 399; — red, 394; — red brown, 436; — violet, 546; — yellow, 403.
- Alkalimetry, 751.
- Alkaline chrome mordant, 251.  
 — iron mordants, 265.  
 — pink mordant, 223, 595.
- Alpaca wool, 46.
- Alpha-naphthol, 685.  
 — orange, 520.  
 — sulphonic acids, 687, 688.
- Alpha-naphthylamine, 677, 682, 687.  
 — claret, 682.  
 — sulphonic acids, 688.
- Alsaee green, 628, 629.  
 — grey, 500.
- Alum, 226, 233, 235, 237, 238, 788.  
 — Basic, 227.  
 — Cake (Concentrated or Patent), 224.  
 — Neutral, 227.
- Alumina, 221.
- Aluminate of soda, 223, 595, 789.
- Aluminates, 222.
- Aluminium, 221, 788.  
 — acetate, 229, 234, 461, 481, 789;  
 — arsenate, 224; — bisulphite, 228;  
 — chloride, 227; — chloride-acetate, 232;  
 — hydroxide (hydrate), 221; — hypo-  
 chlorite, 228; — hyposulphite, 228; —  
 mordants, 232, 461, 565, 568, 569, 579, 585,  
 591, 592, 594, 595, 599, 601, 788; — nitrate,  
 228; — nitrate-acetate, 232; — oxalate,  
 232; — oxide, 221; — phosphate, 224;  
 — salts, 223, 770; — sulphate, 224, 233,  
 235, 236, 238, 585, 599, 601; — sulphate-  
 acetate, 231, 234; — sulphite, 228; —  
 thiocyanide, 229; — tartrate, 232, 237;  
 — thiocyanate, 229; — thiosulphate, 228.  
 — compounds, Analysis and determina-  
 tion of, 788, 864.
- Amaranth, 466, 468, 628.  
 — spirit, 273.
- Amido acid black, 563.  
 — alizarin, 606.  
 — azo benzene, — toluene, 676, 683, 687.  
 — chrysoidine, 683.  
 — diphenylamine, 383.  
 — G acid, 383, 689; — R acid, 689.  
 — naphthol, 683.  
 — black, 563; — ether, 383, 687;  
 — red, 531; — sulphonic acids, 689.
- Amino, see *Amido*.
- Ammonia, 214, 759.  
 — Action of, on cotton, 32.  
 — alum, 224.  
 — Anhydrous, 214.  
 — soda process, 200.  
 — Specific gravity of, 215.
- Ammoniac, Sal, 216.
- Ammoniacal cochineal, 366.
- Ammonium acetate, 217; — bicarbonate,  
 216; — carbamate, 216; — carbonate,  
 216; — chloride, 216; — hydroxide (hy-  
 drate), 214, 759; — oxalate, 217; — salts,  
 214; — sulphocyanide or — thiocyanate,  
 217; — vanadate, 295.
- Amyl alcohol, 300.
- Amyloid, 28.
- Analysis and valuation of materials used in  
 dyeing, 749.  
 — Gravimetric and volumetric, 749.  
 — of colouring matters, 810, 841, 843, 846,  
 847, 848, *et seq.*  
 — of textile fabrics, 859.
- Anhydrous ammonia, 214.
- Animal fibres, 45.
- Aniline, 676, 685, 808; — hydrochloride or  
 — salt, 686, 808, 810; — sulphate, 686.  
 — Diazotisation of, 676.  
 — black, 644; aged, 649, 655; bottomed,  
 656; dyed, 648; Green's, 655, with  
 paraphenylene diamine, 655, 657; Steam-  
 653; topped, 656; Vanadium-, 653.  
 — Composition and constitution of, 645.  
 — Greening of, 655, 656.  
 — Methods of dyeing, on cotton, 648.  
 — on wool and silk, 657.  
 — blue, sol. in spirits, 479; sol. in water,  
 545; — orange, 472; — red, 465; — yel-  
 low, 516.  
 — oil, Aniline salt, see *Aniline*.  
 — spirit, 273.
- Anilime, 685.
- Anisidine, 686.
- Anisoline, 468, 506.
- Annatto, 358.
- Anthra chrome colours, 634.
- Anthraceno, 571.  
 — acid colours, 634, 635.  
 — blue, 605, 606; — brown, 602; —  
 green, 617; — red, 640; — violet, 616;  
 — yellow, 642.  
 — chromate colours, 633, 634.  
 — chrome colours, 634, 635, 636.
- Anthracite black, 560.
- Anthracyl colours, 634.
- Anthraflavone, 672.
- Anthragallol, 602.
- Anthrapurpurin, 577.
- Anthraquinone, 571.  
 — black, 449; — blue, 616; — green,  
 616; — violet, 615.
- Antichlor, 198.
- Antimonic acid, 289.
- Antimonine, 291, 292.
- Antimonious acid, 289.  
 — oxide or Antimony trioxide, 289, 799.  
 — sulphate, 289.
- Antimony, 289, 799.  
 — Analysis of compounds of, 799.  
 — Salts of, 289.  
 — Application of, 291, 460.
- Antimonyl sulphate, 290.
- Apollo red, 529.
- Aqua fortis, 168.
- Archil (see *Orchil*), 363.

- Areca catechu**, 368.  
**Argol** (see *Tartar*), 193, 767.  
**Arnica yellow**, 408.  
**Aromatic compounds**, 684.  
**Arsenate, Aluminium**, 224.  
 — **Ferric**, 264.  
 — **of soda**, 202, 800.  
**Arsenic acid**, 800, 801.  
 — **compounds, Analysis of**, 800.  
 — **Determination of, in fibre**, 866.  
 — **for fixing iron mordants**, 267, 597.  
**Arsenious acid**, 800.  
**Arsenite, Normal solution of sodium**, 783.  
**Artificial fibres**, — silk, 70.  
 — **organic colouring matters**, 375, 841.  
**Auramine**, 473, 474.  
**Aurantia**, 509.  
**Aureolin, Aurolin**, 409.  
**Aureosin**, 503.  
**Auronal colours**, 449.  
**Aurophenine**, 406.  
**Auroposphine**, 472.  
**Autogene black**, 449.  
**Autogenetic colours**, 3.  
**Auxochromous groups**, 4, 376.  
**Azalafne**, 465.  
**Azarin**, 624.  
**Azine green**, 478; — **scarlet**, 470.  
**Azo acid black**, 563; — **blue**, 542, 543;  
 — **brown**, 557; — **carmine**, 531; — **ma-**  
**genta**, 531; — **violet**, 536.  
**Azo black**, 558; — **black-blue**, 683; — **blue**,  
 412; — **bordeaux**, 527; — **brown**, 556;  
 — **carmine**, 535; — **cocoin**, 526, 639;  
 — **corinth**, 427; — **diphenyl blue**, 490;  
 — **eosin**, 520; — **flavin**, 519; — **fuchsine**,  
 531; — **grenadin**, 530; — **merino black**,  
 563; — **patent black**, 563; — **phosphine**,  
 472; — **red**, 529; — **rubin**, 528; — **violet**,  
 425; — **wool violet**, 536; — **yellow**, 519.  
**Azo colours, Analysis of**, 843.  
 — **Insoluble, developed on the fibre**, 673.  
**Azophor black**, 683; — **red**, 678, 680.  
**Azotol**, 683.  
  
**BABLAH**, 185.  
**Back chroming**, 334, 335.  
**Banyan tree**, 367.  
**Baphia nitida**, 300.  
**Barium peroxide**, 220; — **sulphocyanide or**  
**thiocyanate**, 220.  
**Bark, see Quercitron bark**.  
**Barwood**, 360, 835.  
 — **spirit**, 275.  
**Base blue**, 480.  
**Bases**, 192.  
**Basic alum**, 227.  
 — **chromic chloride**, 244.  
 — **colours**, 456, 845.  
 — **Application of, to cotton**, 458, 461,  
 462.  
 — — **to mixed goods**, 464.  
 — — **to silk**, 463.  
 — — **to wool**, 462.  
 — — **Experimental dyeing with**, 740.  
  
**Basic colours, Fastness of**, 458, 463.  
 — — **Methods of dissolving**, 459.  
 — — **Mordanting for**, 459, 478.  
 — — **One bath dyeing with**, 462.  
 — — **Reaction for detecting**, 458.  
 — — **Theory of dyeing with**, 457.  
 — — **Toppling direct cotton colours with**,  
 380, 386.  
 — — **Treatment of, with copper sulphate**,  
 458.  
 — — **cupric acetate**, 284.  
**Basle blue**, 488.  
**Baumé degrees**, 877.  
**Bavarian blue**, 481, 485.  
**Beeswax**, 174.  
**Bengal catechu**, 369.  
**Benzal green**, 476.  
**Benzaldehyde greens, see Malachite, Brilliant,**  
**and Victoria greens**, 476-478.  
**Benzene**, 298.  
**Benzidame**, 685.  
**Benzidine**, 676, 683, 686.  
 — **colours**, 377.  
**Benzine petroleum**, 298.  
**Benzo azurin**, 472; — **black-blue**, 418;  
 — **blue**, 413, 414; — **bordeaux**, 390;  
 — **brown**, 428, 435; — **chrome black**, 442;  
 — **chrome black-blue**, 419; — **chrome brown**,  
 420; — **copper blue**, 418; — **cyanin**, 418;  
 — **dark brown**, 428; — **dark green**, 411;  
 — **fast black**, 441; — **fast blue**, 418; — **fast**  
**grey**, 441; — **fast orange**, 398; — **fast**  
**red**, 390; — **fast scarlet**, 390; — **fast**  
**violet**, 426; — **flavine**, 473; — **green**, 411;  
 — **indigo-blue**, 418; — **navy-blue**, 418;  
 — **nitrol black**, 443; — **nitrol bordeaux**,  
 397; — **nitrol brown**, 430; — **olive**, 411;  
 — **orange**, 397; — **purpurin**, 388; — **rho-**  
**dulin red**, 390; — **scarlet**, 393; — **sky-**  
**blue**, 414; — **violet**, 426.  
**Benzoyl green**, 476.  
**Benzyl black**, 563; — **green**, 555; — **violet**,  
 493.  
**Berries, see Persian berries**.  
**Betanaphthol**, 685.  
 — **Azo-compounds of**, 674, 685.  
 — **orange**, 520.  
 — **sulphonic acids**, 688.  
**Betanaphthylamine**, 677, 682, 687.  
 — **sulphonic acids**, 688, 689.  
**Bi-**, see also *Di-*.  
**Bichromates**, 248, 789.  
 — **as wool mordants**, 255, 337, 568, 631.  
**Bichrome, syn. of Potassium or Sodium**  
*bichromate*.  
**Biebrich acid blue**, 549; — **acid violet**, 537;  
 — **patent black**, 562; — **scarlet**, 523.  
**Binacid potassium oxalate**, 193.  
**Binarsenate of sodium**, 202.  
**Binoxalate of potash**, 193.  
**Binoxalates, see Oxalates**.  
**Bismark brown**, 497.  
**Bistre**, 693.  
**Bisulphates**, 164.  
**Bisulphide of carbon**, 298  
**Bisulphites**, 167, 784.

- Bixa orellana**, 358.  
**Bixin**, 358.  
**Black, Aniline**, see *Aniline black*.  
 — **Chrome-**, 335, 337.  
 — **cochineal**, 365.  
 — **Copperas-**, 334, 335, 336.  
 — **dyeing**, see also under *Logwood*.  
 — — of discharged silk, 342.  
 — — of raw silk, 341.  
 — — of silk, 341.  
 — **liquor**, 261.  
**Blackley blue**, 545.  
**Bleach**, Full and half, of linen, 127.  
**Bleaching**, see also *Discharging and Washing*.  
 — **compounds, Analysis of**, 782.  
 — **kiers**, 90, 100, 101, 111-120.  
 — **liquor**, see *Hypochlorites*.  
 — of cotton, 87.  
 — of hemp, 132.  
 — of jute, 132.  
 — of linen, 126.  
 — of silk, 156, 160.  
 — of souple silk, 156.  
 — of tussur silk, 162.  
 — of wool, 149.  
 — **powder**, 218, 782.  
**Bleeding of colours**, 747.  
**Bleu de lumière, de nuit**, 480.  
**Blue**, see also *Aniline Blue, Soluble Blue, &c.*  
 — **black B**, 558; — **developer A N**, 383; — **for cotton**, 545; — **for printing**, 490; — **green**, 554; — **P B-C**, 622; **Prussian** —, 265, 695; — **stone**, see *Cupric sulphate*; — **verdigris**, 284; — **vitriol**, see *Cupric sulphate*.  
**Boiled-off liquor**, 156.  
**Boiling and evaporation**, 878.  
**Boiling-off silk**, 155.  
**Bombay catechu**, 368.  
**Bonsor's black**, 337.  
**Borax or Borate of sodium**, 204.  
**Bordeaux**, 528, 530.  
**Botany wool**, 46.  
**Bowking**, 88.  
**Bowl spirit**, 273.  
**Brasilein, Brasilin**, 359.  
**Brazil wood**, 359, 835.  
**Breaking of flax**, 42.  
**Bright green**, 475.  
**Brightening (silk)**, 64.  
**Brilliant acid carmine**, 531; — **acid green**, 555;  
 — **alizarin blue**, 625; — **alizarin bordeaux**, 604; — **alizarin cyanin**, 606; — **arohil**, 530; — **azurin**, 413; — **benzo blue**, 411;  
 — **benzo green**, 414; — **black**, 557; — **bordeaux**, 532; — **chrome black**, 635; — **carmin**, 528; — **cochineal**, 523; — **congo**, 388; — **creyl blue**, 487; **crocein**, 525;  
 — **galloocyanine**, 622; — **geranin**, 395;  
 — **green**, 478; — **milling blue**, 550;  
 — **nulling green**, 555; — **orange**, 521;  
 — **purpurin**, 389; — **rhoduline**, 470;  
 — **scarlet**, 522, 525; — **sulphone azurin**, 542; — **sulphone violet**, 537; — **wool blue**, 550; — **yellow**, 405, 519.  
**Broad washing machine**, 141.  
**Bronze liquor**, 693.  
**Buff, Iron**, 694.  
**Buffalo rubin**, 527.  
**Burrs**, 151.  
**Byssus**, 69.  
**CACHOU de Laval**, 449.  
**Cactus opuntia**, 365.  
**Casalpinia**, 359.  
**Cake alum**, 224.  
**Calcium acetate**, 220, 764; — **carbonate**, 219; — **chloride**, 218; — **hydroxide** (— **hydrate**), 218; — **hypochlorite**, 218, 782; — **oxide**, 217; — **sulphate**, 218; — **sulphocyanide or thiocyanate**, 220.  
**Camel's hair**, 46.  
**Campeachy wood**, 330.  
**Camwood**, 360, 835.  
**Cannela**, 497.  
**Capillary analysis**, 846.  
**Capri blue**, 487.  
**Caput mortuum**, 259.  
**Carbamic acid**, 216.  
**Carbazol yellow**, 402.  
**Carbide black**, 446.  
**Carbolic acid**, 684.  
**Carbon bisulphide**, 298; — **tetrachloride**, 298.  
**Carbonising**, 31, 54, 151.  
**Cardinal**, 466, 468; — **red**, 527.  
**Carmin, Indigo**, see *Indigo extract*.  
**Carmine acid**, 365.  
**Carmoisin**, 528.  
**Carnotine**, 409.  
**Carthamin**, 358.  
**Carthamus tinctoria**, 358.  
**Cashmere black**, 563.  
 — **wool**, 46.  
**Castor oil**, 175, 206, 208, 301.  
**Catechin**, 183, 369.  
**Catechol**, 179.  
**Catechu**, 368, 841.  
 — **Black on silk with**, 345.  
**Catechutannic acid**, 183, 369.  
**Cattu italiano**, 449.  
**Caustic potash**, 192.  
 — **soda**, 194, 757.  
 — — **Normal solution of**, 753.  
**Celestine blue**, 621.  
**Cellulose**, 25, 26.  
**Centinormal solutions**, 750.  
**Centrifugal machine**, see *Hydro extractor*.  
**Cerasin**, 528.  
**Cerise**, 466, 468.  
**Cerium**, 296.  
**Cerulein**, see *Coerulein*.  
**Chappe silk**, 61.  
**Chemicals**, 163.  
**Chemicking**, 103.  
**Chestnut extract**, 185.  
**Chicago blue**, 414, 416; — **orange**, 400.  
**Chili saltpetre**, see *Sodium nitrate*.  
**China blue**, 545.  
 — **grass**, 44.

- Chloramine brown, 429; — green, 412; — orange, 401; — violet, 426; — yellow, 405.  
 Chlorantine brown, 437; — lilac, 428; — red, 393; — yellow, 407.  
 Chlorazol blue, 424; — brown, 437; — green, 412; — yellow, 407.  
 Chloride of lime, potash, or soda, see *Calcium, Potassium, or Sodium hypochlorite*.  
 Chlorides, 168.  
 Chlorin, 628.  
 Chlorinating of wool, 56, 151.  
 Chlorine, Action of, on cotton, 38; on jute, 44; on wool, 57, 551.  
 Chloroanisidine P, 682.  
 Chlorophenine orange, 401; — yellow, 405.  
 Chromanile black, 444; — brown, 431.  
 Chromate, Red, syn. of *Potassium bichromate*. — black, 632, 636; — of lead, 690; — method, 633.  
 Chromates, 248.  
 Chromazone red, 530.  
 Chrome, syn. of *Potassium or Sodium bichromate*. — alum, 242; — black, 335, 337; — brown, 556; — fast colours, 634; — fast yellow, 642, 643; — green, 692; — mordants, 251; — orange, 691; — patent green, 637; — violet, 496; — yellow, 642, 690.  
 Chromic acid, 248, 790; as a wool mordant, 255. — anhydride, 248. — compounds, see also under *Chromium*.  
 Chromine, 408.  
 Chromite of soda, 251.  
 Chromites, 240.  
 Chromium, 239, 789; see also *Chromic acid and Chromic anhydride*. — acetate, 246, 791; — arsenite, 246, 692; — bisulphite, 245; — chlorate, 244; — chloride, 244; — chloride-acetate, 247; — chromate, 250; — fluoride, 244, 255, 384, 632; — hydroxide (— hydrate), 240; — monoxide, 239; — mordants, 251; — mordants (M.L.B.), 250, 253; — nitrate, 244; — nitrate-acetate, 247; — oxide, 239; — phosphate, 246; — salts, 241; — sesquioxide, 239; — sulphate, 241; — sulphate-acetate, 247; — sulpho-cyanide or thiocyanate, 245; — trioxide, 248; — tungstate, 296. — compounds, Analysis and determination of, 789, 864. — Application of, 251.  
 Chromocyanine, 622.  
 Chromogene, 4, 375, 637.  
 Chromophor or Chromophorous group, 4, 375.  
 Chromotrop, 632, 633, 634.  
 Chrysamin, 401, 402.  
 Chrysaniline, 472.  
 Chrysaurein, 520.  
 Chryseolin, 520.  
 Chrysoidine, 471.  
 Chrysoin, 520.  
 Chrysolin, 503.  
 Chrysophenine, 406.  
 Ciba blue, 660; — red, 666; — violet, 661.  
 Citric acid, 172, 768.  
 Citronin, 516, 519.  
 Clayton cloth red, 640; — yellow, 408.  
 Clearing, see *Turkey-red*.  
 Clematine, 496.  
 Close red woods, 360, 835.  
 Cloth red, 638, 639; — scarlet, 644.  
 Coal-tar colours, 375, 841.  
 Cobalt, 295.  
 Coccin, 504, 524.  
 Coccus, 365, 367.  
 Cochineal, 365, 840. — Ammoniacal, 366. — Black, 365. — Indicator, 751. — red, 625; — scarlet, 523, 527.  
 Coerulein (S), 616.  
 Colcothar, 259.  
 Collodion, 29.  
 Colorimeter, Colorimetry, 813.  
 Colour, see also *Colouring matter and Dyes*. — and chemical constitution, 4, 375. — and light, 880. — bearing group, see *Chromophor*.  
 Colours, Adjective —, 2; Autogenetic —, 3; Artificial organic —, 375, 841; Basic —, see *Basic Colours*; Benzidine —, 377; Complementary —, 881; Congo —, 377; Direct cotton —, see *Direct cotton colours*; Mineral —, 690; Mordant —, 3, see also *Mordant colours*; Natural —, 303; Pigment —, 3; Polygenetic —, 3; Substantive —, 2; Tetrazo —, 377.  
 Colouring matters, Analysis and valuation of, — 810. — Behaviour of cotton towards, 40. — of silk, 66. — of wool, 59. — Classification of, 2.  
 Columbia black, 443; — blue, 416; — brown, 431; — fast blue, 417; — fast scarlet, 389; — green, 411; — red, 389; — yellow, 405.  
 Common salt, syn. of *Sodium chloride*.  
 Comparative dye tests, 810.  
 Complementary colours, 881.  
 Compound mordants, 5, 221, 222, 254, 293, 619.  
 Concentrated alum, 224, 788.  
 Conditioning, 49, 62, 863.  
 Congo blue, 413, 414; Brilliant —, 388; — brown, 430; — colours, 377; — corinth, 394; — fast blue, 417; — orange, 397; — red, 387, 388; — rubin, 389; — sky-blue, 414.  
 Coomassie navy blue, 541.  
 Cop, Bleaching of cotton yarn in the, 93. — dyeing machines, 711.  
 Copper, 282, 798, see also *Cupric and Cuprous*. — blue, 543, 632. — mordants, 285, 798, 864. — sulphate or — vitriol, see *Cupric sulphate*. — sulphide, 284.

- Copperas, see *Ferrous sulphate*.  
 — black, 336; — vat, 316.  
 Corchorobastose, 44.  
 Coreine, 621, 622.  
 Correction of water used in dyeing, 80.  
 Corron's dyeing machines, 709, 720.  
 Corvan black, 636.  
 Cosmos red, 387.  
 Cotton, Behaviour of, towards acids, 28.  
 — towards alkalis, 32.  
 — towards micro-organisms and ferments, 41.  
 — towards mordants and colouring matters, 40.  
 — towards oxidising and reducing agents, 38.  
 — towards water, 27.  
 — bleaching, 87, 88, 89, 93, 107, 108, 111, 126, 126.  
 — black, 444; — blue, 546; — brown, 436.  
 — Chemical properties and composition of, 28.  
 — corinth, 394.  
 — Dead or unripe, 24.  
 — Estimation of, in fabrics, 859.  
 — Hygroscopicity of, 25.  
 — Mercerising of, 33, 34.  
 — Physical properties of, 23.  
 — piece goods, Bleaching of, 93.  
 — plant, 23.  
 — purpurin, 389; — red, 387, 388, 396; — rubin, 389; — scarlet, 525; — spirit, 275.  
 — wax, 87.  
 — yarn, Bleaching of, 89, 93.  
 — Counts of, 25.  
 — yellow, 402, 403.  
 Counts of cotton yarn, 25.  
 — of jute or linen yarn, 43, 44.  
 — of silk yarn, 62.  
 — of wool and mohair yarn, 47.  
 Coupling process, 380, 383.  
 Coupier's blue, 490.  
 Cow dung, 217.  
 Crabbing, 145.  
 Cream of tartar, 193, 767.  
 Cresol, 684.  
 Cresyl blue, 487.  
 Crimson, Cochineal, 366.  
 — spirit, 275.  
 Crocein orange, 521; — scarlet, 524, 525, 527.  
 Cross-bred wool, 46.  
 Cross-dye colours, 449.  
 Crumpled fast blue, 620; — yellow, 644.  
 Crystal carbonate, 200, 753.  
 — scarlet, 525; — violet, 494, 843, 845.  
 Crystalline, 685.  
 Cudbear, 363, 837.  
 Cumidine, 686; — scarlet, 522.  
 Cupranil brown, 437.  
 Cupric and cuprous compounds, see also *Copper*.  
 — hydroxide, oxide, salts, 283, 285, 798.  
 Cuprous hydroxide, oxide, salts, 283, 655.  
 Cuprum = Copper, 282.  
 Curouma tinctoria, 357.  
 Curcumin, 519.  
 Curoumin, 357, 407.  
 Curouphenin, 407.  
 Cutch, 368, 841.  
 — Prepared or patent, 369.  
 Cyananthrene, 671.  
 Cyananthrol, 615.  
 Cyanin B, 548.  
 Cyanol, 548; — green and — fast green, 554.  
 Cyanosin, 505.  
 Cyclamin, 505.  
 Cyprus blue, 543, 632; — green, 556, 602.  
 DALLIA, 480, 493, 494, 496.  
 Dark green, 628.  
 Decinormal solutions, 750.  
 Decroline, 199.  
 Dehydrothiocoluidine, 687.  
 Delphin blue, 620.  
 Deltapurpurin, 389.  
 Density, 876.  
 Developed colours, 3, 380, 382.  
 Developers, 383.  
 Dextrin, 846.  
 Di-, see also *Bi*.  
 Diamido-stilbene disulphonic acid, 688.  
 Diamine azo-blue, 416; — black, 439; — blue, 413; — bordeaux, 392; — brilliant blue, 414; — brilliant bordeaux, 392; — brilliant scarlet, 391; — bronze, 434; — brown, 432, 433; — catechin, 433; — outh, 434; — dark green, 410; — developer, 383; — fast blue, 415; — fast red, 391; — fast yellow, 404, 405; — gold, 404; — green, 410; — heliotrope, 425; — nitrazol-brown, 434; — orange, 399; — red, 388, 391; — rose, 395; — scarlet, 390, 391; — sky-blue, 414; — steel blue, 415; — violet, 425; — violet-red, 391; — yellow, 404.  
 Diamineral black, 440; — blue, 414; — brown, 434.  
 Diaminogene (black), 440; — blue, 415; — sky-blue, 415.  
 Diamond black, 634, 635, 654; — brown, 430; — flavin, 643; — green, 637; — phosphine, 472; — yellow, 643.  
 — colours, 634.  
 Dianile black, 445; — blue, 421; — bordeaux, 394; — brown, 435; — dark blue, 421; — dark green, 412; — direct yellow, 407; — garnet, 394; — green, 412; — japonin, 435; — orange, 400; — red, 388; — scarlet, 394; — yellow, 403.  
 Dianisidine, 683, 687.  
 Dianole black, 424; — brilliant red, 393; — diazo blue, 447; — green, 412; — sky blue, 425.  
 Dianthin, 396, 504.  
 Diagine black, 498; — blue, 492; — green, 479.

- Diazo black, 442; — blue, 419; — blue black, 443; — bordeaux, 397; — brilliant black, 443; — brilliant bordeaux, 397; — brilliant scarlet, 397; — brown, 430; — dark blue, 419; — ethyl black, 443; — fast black, 443; — indigo blue, 419; — nitrol black, 443; — red-blue, 419; — rubine, 397; — violet, 427.  
 — compounds, 673.  
 Diazotising, 380, 382, 676.  
 Diazurin, 419.  
 Digallic acid, 181.  
 Dinitro-alphanaphthol, 516.  
 Dinitroso-resorcin, 628.  
 Dioxin, 630.  
 Dioxyanthraquinone, 573.  
 Dioxynaphthalene, 685.  
 — sulphonic acid, 688.  
 Dioxynaphthoquinone, 625.  
 Dioxyrubine, 392.  
 Diphenyl blue, 422; — blue-black, 446; — brown, 437; — catechin, 437; — chrysoin, 408; — citronin, 407; — fast black, 446; — fast brown, 437; — fast yellow, 408; — green, 412; — orange, 400, 519; — red, 393; — red-brown, 437; — violet, 428.  
 Direct black, 447, 657; — blue, 422; — blue-black, 442; — bordeaux, 394; — brown, 432, 436.  
 — colours, 3.  
 — cotton colours, 377, 893.  
 — Application of, 379.  
 — Constitution of, 377.  
 — Coupling of, 380, 383.  
 — Diazotising and developing of, 380, 382.  
 — Experimental dyeing with, 739.  
 — Fastness of, 379.  
 — Purification of water for dyeing with, 80, 379, 381.  
 — Topping of, with basic colours, 380, 385.  
 — Treatment of, with formaldehyde, 385.  
 — — with metallic salts, 380, 384.  
 — — with Solidogene, 385.  
 — deep black, 441; — fast yellow, 405; — green, 412; — grey, 445; — indigo-blue, 422; — orange, 400; — rose, 395; — scarlet, 392.  
 — logwood black, 335, 337.  
 Discharged silk, Black dyeing of, 342.  
 Discharging of silk, 155.  
 — of tussur silk, 161.  
 Dissolving of colours, 724.  
 Disulphine blue, 549.  
 Divi-divi, 185.  
 Dolly, 143.  
 Domingo alizarin and — chrome colours, 634.  
 Double antimony fluoride, 290.  
 — brilliant scarlet, 522, 526.  
 — muriate of tin, 273, 796.  
 — oil of vitrol, 163.  
 — salts of antimony, 290, 292, 800.  
 — scarlet, 526.  
 Drèze's dyeing machine, 703.  
 Drugs, Dyers', 163.  
 Drying machines, 731.  
 — of textile goods, 731.  
 — oils, 174.  
 Dung (cow dung), 217.  
 — salty · Dung substitute, see *Sodium arsenate*.  
 Dyeing bath, 247.  
 Dye- and Dyestuff, see also *Colour and Colouring matters*.  
 — tests, 739, 810.  
 — vats or — vessels, 697.  
 — for indigo dyeing, 318, 321, 711.  
 Dyeing, 1, 4.  
 — and saddening method, 7.  
 — Experimental, 739, 810.  
 — Foam, 765.  
 — in the indigo vat, 314, 711.  
 — in mechanical apparatus, 698, 704, 711.  
 — of cops, 711.  
 — of hanks, 705, 707.  
 — of loose fibres, 697, 703.  
 — of piece goods, 717.  
 — of tops and slubbing, 704.  
 — of warps, 709.  
 — of yarn, 705, 707, 709, 711.  
 — Operations after, 726.  
 — Theory of, 8.  
 Eau de Javelle, 192.  
 Eau de Labarraque, 202.  
 Eboli blue, 419; — green, 412.  
 Ecarlate, 504.  
 Eclipse colours, 449.  
 Eoru silk, 157.  
 Elaidic acid, 174.  
 Ellagic acid, 181.  
 Ellagitannic acid, 183.  
 Emerald green, 478.  
 Emeraldine, 646, 647.  
 Emetic, see *Tartar emetic*.  
 Emin red, 640.  
 Emulsion process, 583.  
 Emulsive oil, 301.  
 English black on silk, 342.  
 Eosin, 503, 504; — lakes, 500; — orange, 503; — scarlet, 504.  
 Eosins and Rhodamines, 496.  
 — Application of, 500.  
 — Behaviour of, towards reducing agents, 499.  
 — Constitution of, 499.  
 — General reactions of, 499.  
 Epsom salt, 221.  
 Era black, 635.  
 Eria silk, 69.  
 Erika, 395.  
 Erio chrome colours, 634, 635, 636.  
 — carmine, 531; — cyanine, 549; — — glaucine, 548; — rubine, 531.  
 Erythrin, 504, 505.  
 Erythrosym, 362.  
 Essain, 629.  
 Ether, 300.  
 Ethers, Glycerin, of fatty acids, 174, 300.

- Ethoxy benzidine, 687.  
 Ethyl alcohol, 298.  
 — black, 583; — blue, 481; — eosin, 504;  
 — green, 478; — betanaphthylamine, 383,  
 687; — purple, 484.  
 Ethylene blue, 484.  
 Evaporation and boiling, 878.  
 Experimental dyeing, 739, 810.  
 Extract of indigo, 326, 829.  
 Extracting (carbonising), 21, 443.  
 — of dyewoods, 724.
- F ACID**, 688.  
 Fabrics, Analysis of, 859.  
 Fast acid bordeaux, 639; — acid eosin, 534;  
 — acid magenta, 531; — acid phloxin,  
 534; — acid scarlet, 531; — acid violet,  
 539, 541.  
 — and loose colours, 743.  
 — black, 490, 498; — blue, 490, 494, 551;  
 — blue for cotton, 487; — blue developer,  
 393; — bordeaux, 639; — brown, 556,  
 557; — chrome black, 635; — cotton  
 blue, 492; — cotton brown, 436; —  
 double scarlet, 523; — green, 478, 554,  
 628; — grey, 497; — light green, 554;  
 — light yellow, 517, 518; — milling red,  
 639; — mordant yellow, 643; — neutral  
 violet, 495; — red, 527, 528, 529, 639;  
 — scarlet, 523; — sulphone violet, 537;  
 — violet, 535, 536, 618; — wool green,  
 555; — yellow, 518.  
 Fastness of colours, 743, 749.  
 Fats, Fatty acids, Fatty oils, 173, 205, 300,  
 778, 781.  
 Fermentation vats, 320.  
 Ferric compounds, see also under *Iron*.  
 — acetate, 264; — acid, 259; — ammonia  
 alum, 226; — arsenate, 264; — chloride,  
 264; — ferrocyanide, 265; — hydroxide  
 (hydrate), 259; — nitrate, 264; — nitrate-  
 acetate, 265; — oxalate, 265; — oxide,  
 265; — phosphate, 264; — potassium ferro-  
 cyanide, 265; — potassium sulphate, 264;  
 — salts, 260; — sulphate, 262, 794; —  
 sulphate-nitrate, 264; — sulphocyanide,  
 264; — tartrate, 265; thiocyanate, 264.  
 Ferriocyanide, Ferrous —, 265; Potassium —,  
 193; Sodium —, 202.  
 Ferrites, 264.  
 Ferrocyanide, Ferric —, 265; Ferric potas-  
 sium —, 265; Potassium —, 193; Sodium  
 —, 202.  
 Ferrous compounds, see also under *Iron*.  
 — acetate, 261, 794; — ammonium sul-  
 phate, 792; — carbonate, 261; — chloride,  
 261; — ferriocyanide, 265; — hydroxide  
 (hydrate), 259; — nitrate, 261; — oxal-  
 ate, 262; — oxide, 259, 792; — salts, 266;  
 — sulphate, 261, 792; — vat, 316; —  
 tartrate, 262.  
 Fibres, Analysis of, in fabrics, 859.  
 — Animal, 45, 60, 67, 69, 859.  
 — Artificial, 70.  
 — Chemical technology of, 21.  
 Fibres, Metallic, 70.  
 — Mineral, 21.  
 — Vegetable, 22, 41, 43, 44, 45, 859.  
 Fibroïne, 63.  
 Ficus religiosa, 367.  
 Fisetin, 357.  
 Flavanthrene, 670.  
 Flavazin, 517, 518.  
 Flavon, 353, 354, 834.  
 Flavindin, 310.  
 Flavon, 350.  
 Flavophosphine, 472.  
 Flavopurpurin, 577.  
 Flax, 41.  
 — Bleaching (Linen bleaching), 126.  
 Fleura de garance, 362.  
 Florida red, 531.  
 Floss silk, 61.  
 Fluorescein, 499, 502.  
 Fluorescent blue, 508.  
 Fluoride, Antimony, 290.  
 — Chromium, 244, 255, 384, 569, 632.  
 Foam dyeing, 705.  
 Formic acid, 169, 256, 765.  
 — colours, 446.  
 Formyl violet, 539.  
 Fuchsia, 496.  
 Fuchsine (Magenta), 464; — S, 533.  
 Full bleach (of linen), 127.  
 Fuscamine, 659.  
 Fuscathrene, 670.  
 Fuel oil, 300.  
 Fustet, 356.  
 Fustic (Old), 349.  
 — (Young), 356.
- G SALT**, 688.  
 Gallacetophenone, 623.  
 Gallamic acid, 621.  
 Gallamine blue, 621.  
 Gallanil violet, 620.  
 Gallanilic indigo, 550.  
 Gallanilide, 620; — blue, 620.  
 Gallates, 180.  
 Gallazine, 622.  
 Gallein, 616.  
 Gallic acid, 180.  
 Gallipoli oil, 301.  
 Gall-nuts or galls, 184.  
 Gallocyanine, 619.  
 Galloflavin, 623.  
 Gallotannic acid, 181, 804.  
 Gambier, 368.  
 Gamma, 629, 630.  
 Gamma acid, 688.  
 — amino naphthol sulphonic acid, 689.  
 Garance, Fleura de, 362.  
 Garanceux, Garancin, 362.  
 Gassing or genapping, 98.  
 Gentian blue, 480.  
 Gentianine, 485.  
 Geranin, 395.  
 Germanium, 466, 468.  
 German or soda vat, 324.  
 Giroflé, 496.



- Glacial acetic acid, 170.  
 Glass wool or spun glass, 70.  
 Glaubersalt or Glauber's salt, 195, 762.  
 Glossing, Silk-, 157.  
 Glycerin, 300, 779.  
 — ethers of fatty acids, 174, 300.  
 Golden orange, 520; — yellow, 520.  
 Graebe and Liebermann's theory of the constitution of dyestuffs, 375.  
 Grain colours, 367.  
 Grassing of flax, 127.  
 Gravimetric analysis, 749.  
 Grease, Estimation of, in fabrics, 863.  
 — Wool-, 135, 139, 212.  
 — Wool in the, 47.  
 Grège (silk), 61.  
 Green P L, 555.  
 — verdigris, 284.  
 — vitriol, 261, 792.  
 Greening of aniline black, 647, 649, 655.  
 — of chrome black, 337, 338.  
 Grenat, 534.  
 Grenadine, 466, 468.  
 Grey acetate of lime, 220.  
 — sour, 103.  
 — washing, 99.  
 Grounding black for cotton, 445.  
 Guaiscol, 179.  
 Guernsey blue, 545.  
 Guignet's green, 240.  
 Guinea green, 553; — red, 531; — violet, 539.  
 Gun cotton, 29.  
  
**HÆMATEYN**, 331.  
 Hematoxylin, 330.  
 Hematoxylon campechianum, 330.  
 Half bleach of linen, 127.  
 Hank dyeing, 706.  
 — washing and drying machines, 726, 729, 732.  
 Hardness of water, 73, 78, 218, 219, 773, 774.  
 Hartshorn, Spirits of, 216.  
 Hawking (piece goods in the vat), 322.  
 Heckling flax, 42.  
 Helindone red, 666.  
 Heliotrope, 426.  
 Helvetia blue, 547.  
 Hemp, 43, 132.  
 Hessian brilliant purple, 393; — brown, 431; — fast ruby, 394; — purple, 393; — violet, 426.  
 Hexamethyl pararosaniline chloride, 493.  
 Hide powder, 804.  
 Hoechst new blue, 547.  
 Hofmann's violet, 493.  
 Homophosphine, 472.  
 Huile lampante, tournante, vierge, 300, 301.  
 Humboldt blue, 480.  
 Hydrazine yellow, 517.  
 Hydrocellulose, 30.  
 Hydrochloric acid, 167, 762.  
 — Normal solution of, 753.  
 — Salts of, 168.  
 Hydro-extracting, — extractors, 728.  
 Hydroferrocyanic acid, 266, 459.  
 Hydrogen peroxide, 296, 786.  
 — Bleaching cotton with, 122.  
 — — silk with, 161.  
 — — tussur silk with, 162.  
 — — wool with, 150.  
 Hydrometers, 876.  
 Hydrosulphite N F, A Z, 199, 785, 873.  
 — Sodium-, 166, 785.  
 — vat, 315, 325, 659, 661, 663, 664, 668, *et seq.*  
 Hydrosulphurous acid, 198.  
 Hygrometers, 880.  
 Hygroscopicity of cotton, 25; of silk, 62; of wool, 49.  
 Hygroscopy, 879.  
 Hypoantimonious acid, 289.  
 Hypochlorite of aluminium, 228; of calcium, 218, 782; of potassium, 192; of sodium, 202.  
 Hypochlorites, Analysis of, 782.  
 Hyposulphite, syn. of *Thioarsenate*, and of *Hydroarsinite*.  
 — of soda, 198.  
 Hyraldite, 199, 785, 873.  
  
**ICE** colours, 673; — red, 678.  
 Identification of dyestuffs on the fibre, 867.  
 Immedial colours, 449, 453.  
 Imperial green, 476; — red, 504; — scarlet, 523.  
 Indamine blue, 491.  
 Indanthrene, 667, 669.  
 — colours, 667; — copper, 672; — green, 671; — orange, 672.  
 Indazine, 489.  
 Indazurin, 423.  
 Indian red, 579; — yellow, 519.  
 Indican, 306.  
 Indicanin, 311.  
 Indicators, 749, 751, 757, 785, 791.  
 Indigene, 490; — blue, 423.  
 Indigo, 303, 659.  
 — Analysis of, 815.  
 — Application of, 314.  
 — Artificial, 313, 659, 666.  
 — Ash in, 829.  
 — blue, 494.  
 — brown, 312.  
 — carmin, see *Indigo extract*.  
 — Constituents of natural, 308.  
 — continuous dyeing machine for cotton pieces, 318.  
 — cultivation, 303.  
 — Detection of, on the fibre, 328.  
 — Estimation of, on the fibre, 329, 865.  
 — extract, 310, 326.  
 — — Analysis of, 829.  
 — — Detection of, on the fibre, 328.  
 — — Red or purple, 327.  
 — green, 311.  
 — indophenol vat, 667.  
 — Manufacture of, 304, 313.  
 — Nitric acid test for, 328.  
 — Plants yielding, 303.

Indigo purpuric acid, 310.  
 — red, see *Indirubin*.  
 — Reduced, or Indigo white, 310, 659.  
 — rich in indigo red, 827.  
 — Soluble, 327.  
 — solution, 659.  
 — substitute, 551.  
 — sulphonic acids, 310, 326, 817, 820, 829.  
 — Synthetic, 313, 659.  
 — vat, 659.  
 — vats, Construction of, 318, 321, 711.  
 — — Preparation of, 315, 320.  
 — Water in, 828.  
 — white or Reduced indigo, 310, 659.  
 — Yellow colouring matter in, 312, 828.

Indigofera, 303.  
 Indigotin, 309, 659, 660.  
 — sulphonic acids, 310, 326, 817, 820, 829.

Indihumin, 312.  
 Indiretin, 312.  
 Indirubin, 312, 418.  
 — Indigo base in, 827.  
 — sulphonic acid, 312.

Indoleamine, 625.  
 Indoleamine, 552.  
 Indoline blue, 492.  
 Indol blue, 492.  
 Indoline, 310.  
 Indophenine B, 490.  
 Indophenol, 666; — white, 666.  
 Induline, 489, 490, 551.  
 Indulines of the naphthalene group, 489.  
 Ingrain colours, 410.  
 Ingrained or grain colours, 367.  
 Injector kier, 100.  
 Insoluble azo-colours, developed on the fibre, 673.  
 Iodide starch paper, 676, 783.  
 Iodine green, 475.  
 Iodococsin, 504.  
 Iriamine, 507.  
 Iris blue, 508.  
 Iron, see also *Ferric and Ferrous compounds*.  
 — alum, 264.  
 — buff, 694.  
 — compounds, Analysis and determination of, 792, 864.  
 — liquor, see *Iron Pyrolignite of*.  
 — mordant, 266, 792, 864.  
 — — Alumina, 266.  
 — Muriate of, 261.  
 — Nitrate of, 262, 267, 269, 834, 341, 343, 344, 354.  
 — Oxide, 259.  
 — Pyrolignite of, 261, 267, 268, 269, 335, 341, 354.  
 — salts, see *Ferric and Ferrous salts*.  
 — Application to the textile fibres, 266.

Isaminol, 416.  
 Isatin, 307.  
 Isatis tinctoria, 303.  
 Isobutyl carbinol, 300.  
 Isodiphenyl black, 446.  
 Isopurpurin, 577.  
 Italian green, 449.

JANUS black, 498; — blue, 492; — bordeaux, 471; — colours, 462, 464; — green, 479; — red, 471; — yellow, 475.  
 Japonic acid, 184, 369, 370.  
 Japonica, Terra, 368.  
 Janne d'Orient, 504.  
 Jet black, 561.  
 Jig winch, 717.  
 Jigger, 721.  
 Jute, 43.  
 — bleaching, 132.  
 — butts or — cuttings, 44.  
 — yarn, Counts of, 44.

KANISFEROL, 313.  
 Kallab's colour analyser, 882.  
 Kambewood, syn. of *Camwood*, 360, 835.  
 Katigene colours, 449.  
 Keratine, 50.  
 Kermea, 367.  
 Kermeas orange, 520.  
 Kier, Cotton bleaching, 90, 100, 111, 114, 115, 117, 118.  
 — Turkey-red clearing, 586.  
 Kiserite, 221.  
 Kition green, 554.  
 Klauder's yarn-dyeing machine, 708.  
 Knopperrn, 184.  
 Koechlin's, H., alkaline chrome mordant, 251.  
 — cotton-bleaching process, 111.  
 Kresotine yellow, 402.  
 Kryogene colours, 449.  
 Kyanol, 685.

LACCALINIC acid, 368.  
 Lac dye, 365, 367.  
 Lachmoid, 751.  
 Lactate, Antimony, 291.  
 Lactic acid, 172, 256, 769.  
 Lactoline, 173, 256.  
 Lævulinic acid, 173.  
 Lakes, 2.  
 Lanafuchsine, 530.  
 Lanacyl blue, — navy blue, 543; — violet, 537.  
 Le Blanc soda process, 200.  
 Lead, 285.  
 — acetate, 287, 346; — chromate, 690, 691; — hydroxide (hydrate), 286; — nitrate, 286; — oxides, 286; — plasters, 286; — salts, 286; — Application to the textile fibres, 287, 346.  
 — Red, — White, 286.  
 Leather brown, 497; — yellow, 472.  
 Lecanora tartarea, 363.  
 Leeds' scheme for the analysis of soap, 780.  
 Leuco-compounds, 375, 457.  
 — indigo, see *Indigo white*, 310.  
 — magenta, 457.  
 — rosaniline, 457, 465.  
 Levuline blue, 490.  
 Ley boil, 103, 107, 111.  
 Libi-Divi, syn. of *Diwi-diwi*.  
 Liebans, 363.

- Light (and colour), 880.  
 — Action of, on dyed colours, 743.  
 — on oleic acid, 174.  
 — blue, 480, 545; — green, 475, 553.
- Lignrosine, 256.
- Ligroïne, 298.
- Lima weed, 363.  
 — wood, 359, 835.
- Lime, 217, 218.  
 — salts, see *Calcium*.
- Linen (see also *Flax*), 41.  
 — bleaching, 126.  
 — yarn, Counts of, 43.
- Linoleic acid, 174, 206.
- Linseed oil, 206, 209, 301, 746, 782.
- Liquor ammoniac, 214, 759.  
 — padding machine, 589.
- Litharge, 286.
- Litmus, 752.
- Logwood, 330.  
 — Ageing or Maturing of, 331.  
 — Analysis of, 829.  
 — Application of, 334.  
 — black on cotton, 334; on silk, 341; on wool, 336.  
 — black, Direct, 335, 337.  
 — blue, 335, 340.  
 — Detection of, on dyed fabrics, 347.  
 — Extract, 333, 831.  
 — purple on cotton, 335.
- Loose fibre, Dyeing of, 697.
- Luteicienne, 504.
- Luteolin, 355.
- Lustre wool, 46.
- Lustreing silk, 158.
- Lye boil, 103, 107, 111.
- Lyon's black (on silk), 343.  
 — blue, 480.
- MACHINERY** used in dyeing, 697.
- Machromin, 349.
- Maclura tinctoria, 349.
- Maclurin, 349.
- Madder, 361, 830.  
 — Application of, 362.  
 — Colouring matters of, 362.  
 — extracts, 362.
- Madras blue, 492.
- Magdala red, 470.
- Magenta, 464.  
 — Acid, 533.  
 — Impure, 468.  
 — New, 468.
- Magnesia usta, 220.
- Magnesite, 221.
- Magnesium, 220.  
 — Compounds of, 220.
- Malachite green, 476.
- Malta grey, 497.
- Manchester brown, 497; — yellow, 516.
- Mandarin, 520.
- Manganate, Potassium, 288.
- Manganese, 287.  
 — bronze or brown, 693.  
 — Compounds of, 287.
- Manilla hemp, 45.
- Marine blue, 485, 494.
- Market bleaching, 107.
- Maroon, 466, 468.  
 — S, 534.
- Mars red, 528.
- Martius yellow, 516.
- Mather kier, 111.
- Mauve, Mauveine, 485.
- Measures, System and Standard units of, 875.
- Mechanical theory of dyeing, 8.
- Mechanically absorbed water, Removal of, 727.
- Melanging, 697.
- Melanthrene, 670.
- Melanogene blue, 449.
- Meldola's blue, 488.
- Melissyl alcohol, 174.
- Melogene blue, 423.
- Melting point, Determination of, 781.
- Mercedised cotton, Behaviour in colouring matters, 35.
- Mercoerising of cotton, 32.  
 — under tension, 34.
- Merino wool, 46.
- Meta-chrome colours and mordant, 633, 634.
- Metadioxybenzene, 684.
- Metagallic acid, 180, 182.
- Metamine blue, 486.
- Metanil yellow, 518.
- Metanilic acid, 688.
- Metanitriline, 683.
- Metantimonio acid, 289.
- Metaphenylene blue, 489.
- Metastannic acid, 278.
- Metasulphites, 167, 197.
- Metatoluidine, 686.
- Metatolylene diamine, 383, 686.
- Methyl alcohol, 298.  
 — blue, 481, 545; — eosin, 503, 504; — green, 475; — indone, 491; — naphthylamine delta sulphonic acid, 689; — orange, 751; — violet, 493, 494.
- Methylated spirits, 300.
- Methylene blue, 484; — green, 479; — grey, 497; — violet, 496.
- Metrical system of weights and measures, 875.
- Mikado brown, 482; — golden yellow, 406; — orange, 398; — yellow, 406.
- Milk of lime, 218.
- Milling (or fulling), 48.  
 — orange, 641; — red, 632; — yellow, 518, 642.
- Mimosa, 408.
- Mimotannic acid, 183, 369.
- Mineral black (on silk), 344.  
 — colours, 690.  
 — fibres, 61.  
 — matter, Estimation of, in fabrics, 864.
- Mohair wool, 46.  
 — yarn, Counts of, 47.
- Monogenetic colours, 3.
- Monohydrate (of sulphuric acid), 163.

- Monopole oil, soap, 178.  
 Monosulphites, see *Sulphites*.  
 Mordant, Alkaline chromo, 251.  
 — iron, 265.  
 — pink, 223, 595.  
 — colours, 3.  
 — Artificial, 563.  
 — Dyeing of, 564.  
 — yellow, 642.  
 Mordants, 4, 169, 788.  
 — Application of aluminium, 232.  
 — of antimony, 291, 460.  
 — of chromium, 251.  
 — of copper, 285.  
 — of iron, 266.  
 — of lead, 287.  
 — of nickel, 295.  
 — of tannin, 186, 459.  
 — of tin, 276.  
 — of titanium, 281.  
 — Behaviour of cotton towards, 40.  
 — of silk towards, 65.  
 — of wool towards, 58.  
 — Compound, 5, 221, 222, 254, 293, 519.  
 — for basic colours, 459.  
 — Influence of, on fastness of colours, 746.  
 — Oil, 173, 461, 565, 579, 581.  
 — Sulphur, 476.  
 Mordanting and dyeing method, 7.  
 — Object of, 4.  
 Moric acid, 349. †  
 Morin, 349, 350.  
 — Mannic acid, 349.  
 Morus tinctoria, 349.  
 Mud, Action of street —, on colours, 743.  
 Muga silk, 69.  
 Muriate of iron, 261.  
 — of tin (Single or double), 273, 796.  
 Muriatic acid, see *Hydrochloric acid*.  
 Muscarine, 486.  
 Myrabolana, 185, 804.  
  
**NANKIN** yellow, 694.  
 Naphthalene acid black, — black, 563; — green, 554; — red, 470; — yellow, 515.  
 Naphthamine blue, 421; — brown, 436; — deep blue, 422; — green, 412; — indigo, 422; — pure yellow, 408; — yellow, 407.  
 Naphthazarin, 625.  
 Naphthazine blue, 552.  
 Naphthine brown, 637.  
 Naphthion red, 529.  
 Naphthionic acid, 688.  
 Naphthogene blue, 417.  
 Naphthol (Alpha- and Beta-), 685.  
 — black, 557, 558; — blue, 666; — blue-black, 558; — green, 555; — red, 528, 529; — sulphonic acids, 687; — yellow, 516, 842.  
 Naphtholates, 685.  
 Naphthoquinone oxime, 629.  
 Naphthyl blue-black, 559.  
 Naphthylamine (Alpha- and Beta-), 677, 687.  
 Naphthylamine black, 559; — brown, 556, 658; — claret, 682; — ether, 383, 687; — pink, 470; — sulphonic acids, 688; — violet, 658; — yellow, 516.  
 Naphthylene blue, 486.  
 Napoleon's blue, 696.  
 Natural colouring matters, 303.  
 Navy blue, 545.  
 Nebheb, 185.  
 Neptune green, 554, 555.  
 Nerogene D, 383.  
 Nerol, 562.  
 Net silk, 61.  
 Neutral alum, 227; — black, 443; — blue, 487, 550; — fast violet, 495; — potassium chromate, 248; — red, 469; — violet, 495.  
 New acridine orange, 473; — blue, 485, 486; — coccoïn, 525; — fast green, 478; — green, 476; — grey, 497; — magenta, 468; — methylene blue, 485; — patent blue, 549; — phosphine, 472; — red, 525; — red process, 594; — toluylene brown, 429; — Victoria blue, 482; — yellow, 519.  
 New Zealand flax, 45.  
 Nicholson's blue, 544.  
 Nickel and — compounds, 294.  
 Night blue, 480, 482, 545.  
 Nigraniline, 647.  
 Nigrisine, 497.  
 Nigrosines, 489, 490, 498, 551.  
 Nile blue, 487.  
 Nitraniline, 686.  
 Nitrate of iron, 262, 267, 269, 334, 341, 343, 344, 794.  
 Nitrates, 168.  
 Nitrazol, 678, 680.  
 Nitric acid, 168, 763.  
 — test for indigo, 328.  
 Nitrite, Sodium, 200.  
 Nitro-alizarin, 607; — cellulose, 29; — phenetidine, 686; — phenine, 408; — toluidine, 686.  
 Nitrosamine red, 678, 681.  
 Nitroso-compounds, 628; — blue, 684; — naphthol, 629.  
 Noils, 47.  
 Non-drying oils, 174.  
 Nopal, 365.  
 Nopalin, 504.  
 Nordhausen sulphuric acid, 166.  
 Normal solutions, 750, 752.  
  
**OAK** bark red, 183.  
 Obermaier's dyeing machines, 698, 705.  
 Oenanthinin, 528.  
 Oil, Estimation of, in fabrics, 863.  
 — mordants, 173, 461.  
 — of vitriol, 163, 760.  
 Oils, Drying and non-drying, 174.  
 — Fatty, 174, 204, *et seq.*, 300, 301.  
 — Unsaponifiable, in soap, 778.  
 Oleates, 174.  
 Oleic acid, 174, 206, 209.  
 Olein, 174, 175.

- Oleine, syn. of *Oleic acid*, 207.  
 Olivanthrene, 671.  
 Olive oil, 206, 209, 300, 565, 581, 594.  
 Omega chrome colours, 634.  
 One-bath method, One dip dyes, 8, 337, 365, 569, 631.  
 Opal blue, 480, 545.  
 Opening rollers, 736.  
 Operations after dyeing, 726.  
 Orange, 519, 520, 521; — red, 522; — spirit, 273.  
 Orcein, 364.  
 Orcein, 527, 557.  
 Orchella weed, 363.  
 Orchil, 363.  
 — Analysis of, 837.  
 — liquor, — paste, 363.  
 — red, 532; — substitute or Archil substitute, 529.  
 — weed, 363.  
 Orcin, Orcinol, 364.  
 Organic colouring matters, Artificial, 375, 841.  
 Organzine (silk), 61.  
 Oriol, 403.  
 Orceillin, 530.  
 Orthodioxycbenzene, 179.  
 Orthonitrophenylpropionic acid, 313.  
 Orthoquinone oximes, 628.  
 Orthotoluidine, 686.  
 Overchromed wool, 56, 257, see also 337.  
 Oxalate of tin, 273, 276.  
 Oxalates, 171, 766.  
 Oxalic acid, 171, 766.  
 Oxamine black, 445; — blue, 420; — bordeaux, 392; — copper blue, — dark blue, 420; — fast red, 392; — green, 412; — maroon, 427; — red, 392; — violet, 427.  
 Oxazines, 486.  
 Oxidation black, 648 (footnote).  
 Oxidizing agents, Action of, on cotton, 38; on silk, 64; on wool, 56.  
 Oxylizarins, 571, 577, 578, 602-606.  
 Oxyanthraflavic acid, 577.  
 Oxycellulose, 33.  
 Oxychlorides, syn. of *Basic chlorides*.  
 Oxychrome colours, 634.  
 Oxydiamine black, 440; — brown, 434; — red, 392; — violet, 425; — yellow, 408.  
 Oxydiaminogene, 441.  
 Oxygenated water, syn. of *Hydrogen peroxide*, 296.  
 Oxyisoanthraflavic acid, 577.  
 Oxyoleic acid, 174.  
 Oxyphenine, 403.
- PADDING machines, 702.**  
 — for Paranitraniline red, 681.
- Painting, 1.**  
 Palatine black, 561; — chrome black, 636; — chrome colours, 634; — red, 529; — scarlet, 523.  
 Palmitates, 173.  
 Palmitic acid, 173, 174, 206.  
 Palmitin, 173, 174, 205, 206.
- Paper yellow, 405.  
 Parachrysaniline, 472.  
 Paradiamine black, 440.  
 Parafamine, 658; — blue, 424; — blue-black, 424; — brown, 438, 658; — indigo blue, — navy blue, 424.  
 Paranitraniline brown, 683.  
 Paranitraniline red or Para red, 678.  
 Paraphenylene blue, 490; — diamine, 658; — violet, 496.  
 Paraphosphine, 472.  
 Pararoslaniline, 465.  
 Paratoluidine, 686.  
 Paratungstate, Sodium, 296.  
 Paris violet, 493.  
 Parma blue, 480.  
 Paste colours, Storing of, 565.  
 — White, 283.  
 Patent alum, 224, 788.  
 — blue, 547; — oucht, 369; — dianil black, 445; — phosphine, 472; — rock scarlet, 396.  
 Peach wood, 359, 835.  
 Pearl ash, syn. of *Potassium carbonate*.  
 Pegu brown, 431.  
 Pelikan blue, 490.  
 Pentamethyl pararosaniline chloride, 493.  
 Peri wool blue, 544.  
 Perkin's violet, 496.  
 Permanent hardness of water, 218, 774.  
 Permanganate, Potassium, 289.  
 — Bleaching cotton with, 123.  
 — method for indigo analysis, 817.  
 — Normal solution of, 792.  
 Permanganic acid, 288.  
 Peroxide of barium, 220; of hydrogen, 296, 786.  
 Persian berries, 355.  
 Petroleum benzine or spirit, 298.  
 — Wool washing with, 141.  
 Phenacetolin, 757.  
 Phenamine blue, 421.  
 Phenetidine, 686; — red, 683.  
 Phenocyanine, 622.  
 Phenol, 684; Phenolates, 684; Phenols, 673.  
 Phenolphthalein, 751.  
 Phenosafranine, 469.  
 Phenylamine black, 563.  
 Phenyl violet, 497.  
 Phenylene black, 563; — brown, 497; — diamine, 686.  
 Philadelphia yellow, 472.  
 Phlobaphenes, 181, 183.  
 Phloroglucin, Phloroglucol, 180.  
 Phloxin, 505.  
 Phosphine, 472.  
 Picraminic acid, 515.  
 Picric acid, 515.  
 Piece drying, 734; — dyeing, 717; — washing, 102, 105, 143, 727.  
 Pied leather, 268.  
 Pigment colours, 3.  
 Pink cutting liquor, 275; — mordant, Alkaline, 223; — salt, 275.  
 Plasters, Lead, 174, 286.  
 Plum spirit, 273, 275.  
 Plumbates, Plumbites, 286.

- Pluto black, 442; — brown, 429.  
 Polychromine, 409, 436.  
 Polygenetic colours, 3.  
 Polyphenyl orange, 401; — yellow, 407.  
 Ponceau, 521, 524.  
 Potash, see *Potassium carbonate* and *Potassium hydroxide*.  
 — alum, 226; Chloride of —, 193, 784;  
 Prussiate of —, see *Potassium ferrocyanide*; — salts, see *Potassium salts*;  
 — vat, 324.  
 Potassium bicarbonate, 192; — bichromate, 248, 789; — carbonate, 192, 757; — chlorate, 192; — chromate, 248, 790; — ferric sulphate, 364; — ferri- and ferrocyanide, 193, 265, 270, 341, 343, 695; — hydroxide or — hydrate, 192, 757; — hypochlorite, 193, 784; — manganate, 288; — oxalate, 193; — percarbonate, 192; — permanganate (see also *Permanganate*), 288; — tartrate, Acid, 193, 767.  
 Prague ice black, 693.  
 Prepared starch, 369.  
 Preparing salt, 276.  
 Primrose & l'alcool, 503, 504.  
 Primula, 423, 404.  
 Primuline, 409; — base, 409, 687; — in-grain colours, 410.  
 Printing, 1; — machine, 724.  
 — Bleaching woolen pieces for, 151.  
 Proof spirit, 299.  
 Protocatechuic acid, 179.  
 Prune, 621.  
 Prussiate, see *Ferri- and Ferrocyanide*.  
 Prussian blue, 265, 270, 341, 343, 695.  
 Pseudo-purpurin, 362.  
 Pterocarpus santalinus, 360.  
 Puce spirit, 273.  
 Pulled wool, 47.  
 Purification of water, 80.  
 — of refuse water, 85.  
 Purple cotton spirit, 275; — fixing liquor, 267; — spirit, 273.  
 Purpurin, 362, 577, 578, 602.  
 Pyoktanin, 493.  
 Pyramine orange, 398; — yellow, 402.  
 Pyrazine yellow, 516.  
 Pyrocatechin, 179.  
 Pyrogallol or Pyrogallic acid, 180.  
 — Derivatives of, 179, 616.  
 Pyrogallolphthalein, 616.  
 Pyrogene colours, 449.  
 Pyrol colours, 449.  
 Pyrolignite of iron, 261, 267, 268, 334, 341, 794.  
 Pyronine, 468.  
 Pyrosin, 504.  
 Pyrosulphite, 167.  
 Pyrotin, 527; — orange, 521.  
 Pyroxylin, 29.  
 Quercetin, 353.  
 Quercitanic acid, 183, 353.  
 Quercitrin, 353.  
 Quercitron bark, 353, 834.  
 Quercus coccifera, 367; — nigra or tinctoria, 353.  
 Quicklime, 217.  
 Quillaya bark, 302.  
 Quinoline yellow, 518.  
 Quinone or Benzoquinone, 375.  
 — oxime, 628.  
 Quintinormal solutions, 750.  
 R SALT, 688.  
 Rain water, 74.  
 Ramie, 44.  
 Rancidity, 174, 301.  
 Rauracienne, 627.  
 Raw silk, 61; — Black dyeing of, 341.  
 Recovery of fatty matter from wool washing, 139, 212.  
 Red-blue, 545.  
 Red chromate, see *Bichromate*; — cotton spirit, 275; — lead, 286; — liquor, 231; — prussiate, see *Ferrocyanide*; — sanders, 360, 835; — spirit, 273; — violet, 537; — woods, 359, 360, 835.  
 Reduced indigo or Indigo white, 310.  
 Reeling of linen yarn, 127; of silk yarn, 61.  
 Refuse water, Purification of, 85.  
 Removal of mechanically absorbed water, 727  
 Reseda luteola, 354.  
 Resin; Determination of, in soap, 779.  
 Resoflavin, 624.  
 Resorcin, 382, 684; — blue, 508; — brown, 557; — yellow, 520.  
 Resorufin, 508.  
 Retting flax, 41.  
 Revolver cylinder (Obermaier apparatus), 705.  
 Rhamnus amygdalinus, 355.  
 Rhamnetin, 356.  
 Rhes, 44.  
 Rheonine, 472.  
 Rhodamines, 488, 498, 505-508.  
 Rhodine, 507.  
 Rhoduline red, 470.  
 Rhus cotinus, 356.  
 Ricinoleic acid, Ricinolein, 174, 205, 206.  
 River water, 75.  
 Road dirt, Action of, on colours, 743.  
 Roccella tinctoria, 363.  
 Roccellin, 527.  
 Rongalite, 199, 785, 873.  
 Rosaniline, 465; — blue, 479.  
 Rosanthrene, 396; — bordeaux, 396.  
 Rosazetin, 505, 507; — scarlet, 507.  
 Rose & l'alcool, à l'eau, 504; — bengale, 505.  
 Roseine, 465.  
 Rosindulines, 489, 535.  
 Rosolane, 496.  
 Rosophenine, 396; — geranin, 395.  
 Rouille, 262.  
 Rubbing boards for linen pieces, 130.  
 Ruberythric acid or Rubian, 362.  
 Rubia tinctorum, 361.  
 Rubidin, 527.  
 Rubin, 465; — Acid, 533.  
 Rubramine, 496.

- Rufanthrene, 671.  
 Rufallic acid, 181.  
 Running or bleeding of colours, 379, 747.  
 Russian green, 628; — red, 460, 468.
- SADDENING, 7.**  
 Safflower, 358.  
 Saffron, Indian, 357.  
 Safraniline, 405.  
 Safranine, 469, 470, 496.  
 — General reaction of, 469.  
 Saffrosin, 504.  
 Sal ammoniac, Sal volatile, 216.  
 Salicine colours, 634, 635; — yellow, 403.  
 Salmon red, 395.  
 Salt (Common), 199; Spirits of, 163, 762.  
 Salts, 192; — of hartshorn, 216; — of sorrel or of lemon, 193.  
 Sandal wood, Sanders (Red), Santal wood, 360, 835.  
 Santalin, 360.  
 Sapan wood, 359, 835.  
 Saponification, 174, 205.  
 — equivalents, 206, 208, 781.  
 Saunders wood, 360, 835.  
 Saxony blue, 327.  
 Scarlet, Cochineal, 365, 523, 527.  
 Scarlets, Azo-, 521-527.  
 Schaeffer's acid, Schoellkopf's acid, 688.  
 Schuetzenberger's salt, 198  
 Scouring, 137.  
 — soap, 212.  
 — value of soap, 782.  
 Scroop (silk), 64.  
 Soutching flax, 42.  
 Sea silk, 69.  
 Seed lac, 368.  
 Seminormal solutions, 750.  
 Serge blue, 545.  
 Sericine, 63, 66.  
 Sericinic acid, 64.  
 Seto-cyanine, -glauine, -paline, 483.  
 Shallow well water, 75.  
 Sheep, Varieties of, 46.  
 — Wool of diseased, 46.  
 Shellac, 368.  
 Sida fibre, 45.  
 Silicate of soda, 203.  
 Silk, 60, 859.  
 — Artificial, 70.  
 — Behaviour towards acids, 63; — alkalis, 64; — colouring matters, 66; — metallic salts, 65; — oxidising agents, 64.  
 — Black dyeing of, with logwood, 341.  
 — Bleaching, 160.  
 — Boiling-off, 156.  
 — Chemical properties of, 63.  
 — Colouring matter of yellow, 66.  
 — Composition of, 63.  
 — Conditioning of, 62, 863.  
 — Discharging and bleaching of, 155.  
 — Eoru, 157.
- Silk, Estimation of, in fabrics, 859, 860.  
 — glossing, 157.  
 — glue, or Silk gum, 64.  
 — Hygroscopicity of, 62.  
 — Lustre, 158.  
 — Physical properties of, 62.  
 — Raw, 61.  
 — Scroop of, 64.  
 — Souple, 156.  
 — stretching, 157.  
 — Tassar, or Tussah, 67, 161.  
 — Varieties of, 60, 67, 69.  
 — Wild, 67.  
 — Wool-, 57.  
 — yarns, 61, 155.  
 — — Counts of, 62.  
 — — Reeling of, 61.  
 Silver grey, 498.  
 Singeing, 94.  
 Single-bath method, 8, 337, 569, 624.  
 — muriate of tin, 278.  
 Slaked lime, 218.  
 Slop padding, 723.  
 Slubbing, 47.  
 Soap, 204; — Analysis of, 776-782; — as a mordant, 461, 501; Cold process of making —, 210; Curd —, 211; Fatty matter in —, 204, 777, 778, 781; Hard —, 206, 210; Neutral —, 211; Potash, Soft or sweat —, 206, 210; Soda —, 206, 210; Softening —, 212; Yellow household —, 211.  
 Soda, see also Sodium, 194, 200, 753, 757; — alum, 226; — ash, 201, 753; Caustic —, 194, 753; — crystals, 200, 753; — vat, 324.  
 Sodium acetate, 204; — aluminate, 223, 595; — arsenate and — binarsenate, 202, 800; — bichromate, 249, 789; — bisulphate, 197; — bisulphite, 197, 784; — carbonate, 200, 753; — chlorate, 202; — chloride, 199, 754; — ferri- and ferrocyanide, 202; — hydroxide or — hydrate, 194, 753, 757; — hypochlorite, 202, 784; — hydrosulphite, 198, 785; — metasilphite, 197, 784; — nitrite, 200, 763; — peroxide, 194, 787; — phosphate, 203; — silicate, 203; — stannate, 276; — sulphate, 196, 762; — sulphide, 448, 762; — sulphite, 197, 755, 784; — sulphoxylate - formaldehyde, 199, 785; — thiosulphate, 198; — tungstate, 296.  
 Soft red woods, 359, 835.  
 Solamine blue, 414.  
 Solferino, 465.  
 Solid green, 476.  
 Solidifying point, Determination of, 781.  
 Soluble aniline blue, 544; — blue, 545; — glass, 203; — oil, syn. of Turkey-red oil; — red woods, 359, 835.  
 Solution (of tin), 275, 797.  
 Solvay soda process, 200.  
 Sorbin red, 198.  
 Sorrel, Salts of, 193.  
 Souple silk, 156; Black on —, 346.  
 Sour, Grey or First, 103; White —, 104.  
 Specific gravity, 870

- Spirits, Methylated, 300; — of hartshorn, 216; — of salt, 167, 762; — of wine, 298; Petroleum —, 298; Proof —, 299; Wood —, 298.  
 Spray dyeing, 6.  
 Spring water, 75.  
 Spun glass or Glass wool, 70.  
 — silk, 61.  
 Square beater washing machine, 104, 105.  
 Squeezing, 728.  
 St. Denis black, 449; — red, 396.  
 Staining, 1.  
 Standard or normal solutions, 752.  
 Stanhope purifier, 82.  
 Stanley red, 640.  
 Stannate of soda, 276.  
 Stannates, 272.  
 Stannic acid, 272; — hydroxide or hydrate, 272; — oxide salts, 274, 275, 276, 797.  
 Stannites, 271.  
 Stannous hydroxide or hydrate, 271; — oxide, 271; — salts, 272, 273, 796.  
 Staple of wool, 47.  
 Steam black, 653.  
 Steaming, 146, 592, 728, 743.  
 Stearates; Stearic acid, Stearin, 173.  
 Steel grey, 498.  
 Stentering, 736.  
 Stick lac, 368.  
 Stilbene orange, 401; — yellow, 406.  
 Stoving of silk, 160; — of souple silk, 156; of wool, 149.  
 Stretching, 142, 157, 736.  
 Stuffing and saddening method, 7.  
 Substantive colours, 2.  
 Substitute for tartar, 194, 197, 768.  
 Suction by vacuum for removal of moisture, 731.  
 Stunt, 134.  
 Sulphamine brown, 637.  
 Sulphanilic acid, 688.  
 Sulphaniline black, 449.  
 Sulphate-acetates, 231, 247.  
 Sulphate-chromate, Basic chromium, 250.  
 Sulphate-nitrate, Ferric, 263.  
 Sulphated oil, syn. of *Turkey-red oil*.  
 Sulphates, 16a.  
 Sulphide colours, 447.  
 — of copper, 284.  
 Sulphine, 409; — brown, 449.  
 Sulphindigotic acid, 310.  
 Sulphites, 167.  
 Sulpho-acetates, syn. of *Sulphate-acetates*.  
 Sulphur acid blue, 542; — azurin, 542; — black, 541; — brown, 557; — cyanin, 541; — cyanin black, 561; — dark brown, 557.  
 Sulphopurpuric acid, 310.  
 Sulphur colours, 447.  
 — dioxide, — trioxide, 166.  
 — mordant, 463, 478.  
 — in wool, 50, 51.  
 Sulphuric acid, 163, 700.  
 — — Fuming or Nordhausen, 166.  
 — — Normal solution of, 752.  
 — anhydride, 166.  
 Sulphuric ether, 300.  
 Sulphurcol colours, 449.  
 Sulphurous acid, 167, 784.  
 Sultan 4 B, 388; — yellow, 406.  
 Sumach, Sumach extract, 184, 185, 804.  
 Sun yellow, 407.  
 Sunn hemp, 45.  
 Superargol, 194.  
 TANNATES, 182.  
 Tannic acid, 181, 802, 804.  
 Tannin, syn. of *Tannic acid*, 181.  
 — — mordants, 184.  
 — — Analysis of, 802-806.  
 — — Application to cotton and linen, 186, 334, 459, 462, 501, 507, 582, 585.  
 — — to mixed goods, 189, 464.  
 — — to silk, 190, 341.  
 — — to wool, 190, 599, 601.  
 — — used in dyeing, 184.  
 Tartar, 193, 767.  
 — emetic, 290, 291, 799.  
 — substitute, 194, 197, 768.  
 Tartaric acid, 172, 767, 768.  
 Tartrazin, 517.  
 Tasar, see *Tussur*.  
 Temporary hardness of water, 219, 774.  
 Tentering, 736.  
 Terra-cotta, 436.  
 Tetrabromesorufin, 508.  
 Tetrachloride of carbon, 298.  
 Tetrasilicate of sodium, 203.  
 Theory of dyeing, 8.  
 Thermometers, 877.  
 Thiamine red, 392.  
 Thiazine, 484; — red, 392.  
 Thiazol yellow, 408.  
 Thiocarmine, 550.  
 Thiocatechin, 449.  
 Thiochromogen, 409.  
 Thiodiphenylamine, 484.  
 Thioflavin, 409, 474.  
 Thiogene colours, 449.  
 Thioindigo red, 661; — scarlet, 665.  
 Thioindoxyl, 662.  
 Thion colours, 449.  
 Thional colours, 449.  
 Thionaphthene indigo, 662.  
 Thionine, 484; — blue, 485.  
 Thionol colours, 449.  
 Thiophenol black, 449.  
 Thiorubin, 392.  
 Thioxine colours, 449.  
 Tin, 271.  
 — compounds, Analysis of, 796.  
 — Application of, 276.  
 — crystals, 272, 796; — mordants, 276; Muriate of —, 273; Nitrate of —, 273; Oxalate of —, 273, 276; Oxides of —, 271, 272; Oxymuriate of —, 274; — salt, 272; Solution of —, 275, 796, 797; — spirits, 273, 275, 796.  
 Tinting, 1.  
 Tintometer, 814.



- Titan black, 447; — blue, 424; — brown, 438; — como, 424; — ingrain blue, — navy, 424; — orange, 401; — pink, 395; — red, — scarlet, 392, 393; — yellow, 404, 408.  
 Titanium compounds, 279, 798.  
 Titanous chloride, 280, 798; — for analysis of colouring matters, 843.  
 Tolan red, 531.  
 Toledo blue, 420.  
 Tolidine, 676, 678, 683, 687.  
 Toluidine, 676, 678, 686; — blue, 485.  
 Toluylene blue, 491; — brown, 429; — diamine, 383, 686; — orange, 398; — red, 393, 469; — yellow, 403.  
 Top dyeing, 704.  
 Topping with basic colours, 380, 385, 452.  
 Tops (wool), 47.  
 Trame (silk), 61.  
 Tramping and wringing machine, 584.  
 Triamidophenol, 516.  
 Trianisoline, 507.  
 Triazol blue, 421; — brown, 435; — deep blue, 421; — fast red, 395; — indigo blue, 421; — red, 395; — violet, 427; — yellow, 407.  
 Trinitrophenol, 515.  
 Trioletin, see *Olein*, 174.  
 Trioxanthraquinone, 577, 602, 603.  
 Trioxybenzoic acid, 180.  
 Trioxybenzophenone, 623.  
 Tripalmitin, see *Palmitin*, 173.  
 Triphenylmethane, 456.  
 Triphenylrosaniline and Triphenylpararos-aniline chloride, 479.  
 Tristearin, see *Stearin*, 173.  
 Trisulphone blue, 423; — brown, 438; — violet, 428.  
 Trona red, 396; — violet, 426.  
 Tropaeolin, 519, 520.  
 Tungstates, Tungsten, 296.  
 Turkey red, 579.  
 — dyeing processes, 583, 586, 590, 591.  
 — Theory of, 580.  
 — oil, 175, 581, 806.  
 — as a mordant for basic colours, 461.  
 — processes for alizarin dyeing, 590, 591.  
 Turmeric, 357, 835.  
 Turquoise blue, 484.  
 Tussah, see *Tussur*.  
 Tussur, 67, 862.  
 — Black dyeing, with logwood, 347.  
 — Bleaching and discharging, 161.  
 Twaddle's hydrometer degrees, 877.  
  
 UNCARIA gambier, 369.  
 Union black, — blue, — brown, 447.  
 — fast claret, 532.  
 Unripe cotton, 24.  
 Urania blue, 552.  
 Uranin, 502.  
 Uranium, Uranium sulphate, 296.  
 Urine, 216.  
 — vat, 324.  
  
 VACANŒYNE blue, 492.  
 Valonia, 185.  
 Valparaiso weed, 363.  
 Valuation of materials used in dyeing, 749.  
 Vanadium and Vanadium compounds, 295, 653.  
 Variolaria orcina, 368.  
 Vat dyeing, 314, 452, 659-673.  
 Vat red B, 686.  
 Vegetable fibres, 22.  
 Verdigris, 284.  
 Vermilionettes, 500.  
 Vert étincelle, Vert de methylaniline, Vert lumière, 474.  
 Vesuvine, 497.  
 Victoria black, 560; — blue, 481, 482; — green, 476, 478; — pure blue, 482; — rubin, 528; — violet, 536; — yellow, 519.  
 Vienna wool, 46.  
 Vidal black, 449.  
 Vinegar, 170.  
 Violamin, 541.  
 Violanthrene, 671.  
 Violet (Basic), 493, 494.  
 Virgin oil, 300.  
 Viridanthrene, 671.  
 Vitriol, Blue, 283; Green —, 261; Oil of — 163; White —, 293.  
 Volatile liquids, 298, 300.  
 — Wool washing with, 140.  
 Volumetric analysis, 749.  
  
 WARP drying, 733.  
 — dyeing, 709.  
 — silk, 61.  
 Wash stocks, 92.  
 Washing (and Bleaching), 87.  
 — after dyeing, 726.  
 Waste liquors, Recovery of fatty matter from, 139, 212.  
 Water, 73, 769.  
 — Action of, on cotton, 27; on jute, 44; on silk, 62, 63; on wool, 49, 53.  
 — Analysis of, 76, 769.  
 — blue, 545.  
 — Classification of natural, 74.  
 — Correction of, 80, 379, 450, 458.  
 — for bleaching, washing, and scouring, 78.  
 — for boiler purposes, 77.  
 — for dyeing and mordanting, 79.  
 — Hardness of, 75, 77, 218, 219, 773, 774.  
 — Purification of, 80.  
 — Testing for technical purposes, 76.  
 West silk, 61.  
 Weighting of black silk, 341.  
 Weights, System and standard units of, 875.  
 Weingartner's tables for analysis of coal-tar colours, 848.  
 Weld, 354.  
 Well water, 75.  
 White paste, 283.  
 — sour for cotton piece goods, 104.  
 — vitriol, 293.  
 Wild silks, 67.  
 Wilson's bleaching liquor, 228.

- Wine, Spirits of, 298.  
 Witt's theory of dyeing, 13.  
 — of the constitution of organic dye-  
 stuffs, 373.  
 Wood plant, 303.  
 — vat, 320.  
 Wooded shades, 314, 340.  
 Wood spirit, 298.  
 Woods, Red, 359, 835.  
 Wool, 45.  
 — Behaviour of, towards acids, 54; al-  
 kalies, 55; colouring matters, 59; heat,  
 50; metallic salts, 58; oxidising agents,  
 56; water, 53.  
 — black, 561, 563.  
 — bleaching, 149.  
 — blue, 550.  
 — Chemical properties and composition of,  
 50.  
 — Chlorinating of, 57, 151, 551.  
 — Conditioning of, 49, 863.  
 — Diseased sheeps', 46.  
 — Estimation of, in fabrics, 859, 860.  
 — grease, 134, 139, 213.  
 — green, 555.  
 — Hygroscopicity of, 49.  
 — Impurities of raw, 134.  
 — in the grease, 47.  
 — Overchromed, 56, 257.  
 — Physical properties of, 49.  
 — Pulled, 47.  
 — red, 528, 532; scarlet, 527.  
 — scouring (or washing), 134.  
 — sorting, 135.  
 — Structure of, 45, 47.  
 — washing, 134.  
 — — Loose, 134.  
 Wool washing, Bye-products of, 139, 212  
 — — with volatile liquids, 140.  
 — — Pieces, 143.  
 — — Yarns, 141.  
 Wringing, 728.  
 XANTHORHAMNIN, 356.  
 X L acid eosin, red, 535.  
 Xylidine, 676, 688; — scarlets, 522, 523.  
 YAMAMAI silk, 69.  
 Yarn, Counts of, 25, 43, 44, 47, 62.  
 — drying, 732.  
 — dyeing, 705.  
 — — machines, 584, 707-709.  
 — Stretching frame for worsted, 142.  
 — Washing and bleaching, 89, 127, 141,  
 149, 155, 161.  
 Yellow chromate, see *Potassium chromate*.  
 — household soap, 211.  
 — prussiate, see *Ferrocyanide*.  
 — silk, Colouring matter of, 66.  
 — T, 520.  
 Yolk, 50, 134, 213.  
 Yorkshire fat or grease, 140, 213.  
 Young fustic, 356.  
 ZAMBESI black, 444; — blue, 417; —  
 brown, 431; — sky-blue, 417.  
 Zinc and zinc compounds, 292, 801.  
 — as mordants, 461.  
 — dust or zinc powder, 293, 801.  
 — vat (Zinc lime vat), 317.  
 Zittau dyeing machine, 703, 715.





