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CHEMISTRY

OF THE

ORGANIC DYESTUFFS.

BY

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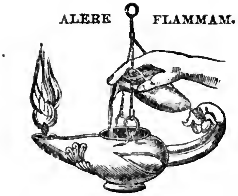

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AUTHOR'S PREFACE.

About three years ago I wrote an article for Ladenburg's 'Handwörterbuch der Chemie,' containing in a concise form an exhaustive account of the history of the Organic Dyestuffs. This article was also published separately, and its good reception induced me to produce the present work, which I have based as far as possible upon the earlier one.

The article in question was not complete in itself, and in the present instance certain sections which came under other headings in the 'Handwörterbuch' have been added. New material has also been supplied through the advances made in the coal-tar colour industry and in our scientific knowledge of the constitution of dyestuffs during the last three years. Again, some subjects have been dealt with at a greater length than was permitted by the somewhat limited space of the 'Handwörterbuch.' Consequently, the subject-matter of the earlier work has been submitted to a thorough revision, and the systematic classification of dyestuffs into natural chemical groups attempted in the original book has been carried out in a more complete manner, owing to the advances made in our knowledge of their constitution.

The present work cannot therefore be regarded as a second edition of the article from the 'Handwörterbuch,' and as I have sought to give the whole the form of a small chemical handbook, dealing with dyestuffs from a scientific standpoint, I have selected 'The Chemistry of the Organic Dyestuffs' as a suitable title.

In this work, as in the previous one, considerable weight has been laid upon the relationships existent between the constitution and tinctorial properties of the dyestuffs.

I have thought it advisable to deal only with the principles involved in the manufacture of individual dyestuffs, as details for their technical production are unreliable, owing to the continuous developments taking place in the industry in question.

The application of dyestuffs to textile fibres has been dealt with rather more fully than in the earlier work, but not at a greater length than is in accordance with the character of the book. To technologists requiring further details of the application of dyestuffs I can recommend Hummel's excellent work on 'The Dyeing of Textile Fabrics.'

Basle, October 1888.

TRANSLATORS' PREFACE.

LITTLE remains for us to add to Prof. Nietzki's account of the design and character of his book. It has met with very general appreciation in Germany, and this made us think that a translation might be of service to English workers in the field which the book covers.

Some time has elapsed since the original appeared, and we have attempted as far as possible to bring the subject-matter up to date. New colouring-matters have been introduced without altering Prof. Nietzki's method of classification, a method which has been very generally adopted since its appearance. In some cases (Primuline, Thioflavine; Pyronine, &c.) new sections might have been desirable; we preferred, however, to leave the book in its original form.

The figures in the text apply to the references given on pages 273–288. The references have been left as in the original, with the one exception that, wherever possible, the English-Patent number has been added.

Our thanks are due to the Directors of the Farbwerke Höchst (Meister, Lucius, and Brüning) and of the Farbenfabriken, vormals F. Bayer and Co., Elberfeld, for the ready kindness with which they placed ample information at our disposal.

Paisley, May 1892.

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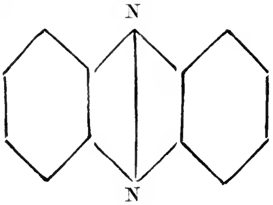
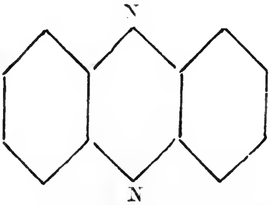
ERRATA.

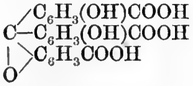
P. 9. Phenazine formula, *read*



instead of

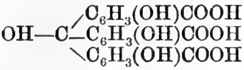


P. 41. *For* Symmetrical Amidoazobenzene *read* Symmetrical Diamidoazobenzene.
P. 54, line 22, *for* Tropäolin OOO No. 1 *read* Tropäolin OOO No. 2.
P. 134. Formula for Chrome-Violet should be



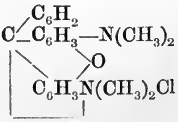
$$\begin{array}{l} \quad\diagup \mathrm{C_6H_3(OH)COOH} \\ \mathrm{C}-\mathrm{C_6H_3(OH)COOH} \\ |\ \diagdown \mathrm{C_6H_3COOH} \\ \mathrm{O}\diagup \end{array}$$

instead of



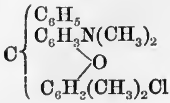
$$\mathrm{OH}-\mathrm{C}\begin{array}{l} \diagup \mathrm{C_6H_3(OH)COOH} \\ - \mathrm{C_6H_3(OH)COOH} \\ \diagdown \mathrm{C_6H_3(OH)COOH} \end{array}$$

P. 136. Rosamine formula should be



$$\begin{array}{l} \quad\diagup \mathrm{C_6H_2} \\ \mathrm{C}-\mathrm{C_6H_3}-\mathrm{N(CH_3)_2} \\ |\ \diagdown \qquad \diagdown \mathrm{O} \\ |\qquad \mathrm{C_6H_3N(CH_3)_2Cl} \\ |\_\_\_\_\_\_\_\_| \end{array}$$

instead of



$$\mathrm{C}\begin{cases} \mathrm{C_6H_5} \\ \mathrm{C_6H_3N(CH_3)_2} \\ \quad \rangle \mathrm{O} \\ \mathrm{C_6H_3(CH_3)_2Cl} \end{cases}$$

INTRODUCTION.

CERTAIN chemical bodies possess the property of only transmitting or reflecting certain constituents of white light, while the others are absorbed. In other words, such bodies have a particular colour, more or less characteristic. These bodies occur amongst the so-called chemical elements, and the colour of the same element may be totally different according to the form and state of aggregation under which it is observed. Certain elements (*e.g.* chromium) always form coloured compounds; with others, again, the coloration of the compounds may be regarded as an exception, and if not caused by combination with a colour-giving element, depends on the constitution of the compound.

Coloured carbon compounds come under the latter classification.

The number of organic compounds containing, besides carbon, hydrogen, oxygen, and nitrogen is very large, and by far the greater number of them are colourless. On the other hand, some compounds of carbon with these elements possess colour which far surpasses that of any other element, both as regards intensity and character.

The coloured carbon compounds often differ little, or not at all, from the colourless ones in their percentage composition, and it is this fact which renders it certain that it is the structure of the compounds which causes in one case colour, in the other none.

In the life-processes of plants and animals both colourless and coloured carbon compounds are formed, and the latter have been employed since the earliest periods as dye-materials.

Natural dyestuffs have for many years been the subjects of thorough chemical investigation, but their study has afforded little knowledge as to the general nature of coloured carbon compounds; and it is only since dyestuffs have been prepared synthetically that we have gradually come to understand the constitution of the greater number of these bodies.

Very little is known of the primary cause of colour in such compounds, but our knowledge is so far advanced that colour is regarded as a characteristic property of whole classes of chemical compounds; and the study of the constitution of such compounds has shown that a close relationship exists between their colour and their chemical structure.

A study of the carbon compounds shows that compounds of carbon with one or with several elements of equal valency are all colourless. For example, all hydrocarbons are colourless, and derivatives obtained by the introduction of monatomic elements are also colourless.

Colour in coloured compounds depends on the introduction of compound radicals, mostly polyvalent; but at the same time a certain building-up of carbon atoms in the molecule is necessary for production of a real colouring-matter. For the latter reason, nearly all organic dyestuffs belong to the aromatic series, and are derivatives of benzene, naphthalene, anthracene, or quinoline. The radicals which possess this power of producing colour in a hydrocarbon show a characteristic behaviour towards nascent hydrogen.

Nascent hydrogen possesses the property of converting coloured carbon compounds into colourless ones with greater or less facility; the reaction which takes place may, however, be widely different in various cases. The nitro-group is converted into an amido-group, and on oxidation the nitro-group cannot be reproduced. The azo-group is converted in a similar manner into two amido-groups, but as an intermediate stage of the reaction hydrazo-compounds are formed.

These hydrazo-compounds may be regarded as types of a class of colourless bodies, termed leuco-compounds. A large number of dyestuffs yield these leuco-compounds on reduction. These new bodies mostly contain two atoms of hydrogen more than the dyestuffs, and are converted into the latter on oxidation.

This circumstance was made a subject of study by Graebe and Liebermann (Ber. i. p. 106); and in 1867 a theory was advanced assuming the presence of a bond between the colour-giving groups in dyestuffs yielding leuco-compounds, corresponding to the linkage of the oxygen atoms in quinone in the constitutional formula accepted at that period. In 1876 Otto N. Witt published a more complete theory of the nature of colouring-matters, and this theory may be comprised in the following general laws (Ber. ix. p. 522).

The colour of a compound depends on the presence of a certain group of atoms, which is therefore termed a colour-giving group or chromophor.

The introduction of this chromophor produces a more or less intensely coloured body, which, however, is not a dyestuff; and the dyestuffs are only formed by introduction of one or more radicals capable of imparting salt-forming properties, which may be acid or basic. Witt terms compounds which only contain a chromophor, chromogens.

Before proceeding it is necessary, however, to define the difference between a coloured body and a dyestuff somewhat more clearly. A real dyestuff is a body which possesses, besides colour, the property of communicating colour to fibres, especially to animal fibres, doing this by reason of a certain peculiar affinity betwixt the colouring-matter and the fibre. If a silk skein is placed in a solution of dyestuff, it gradually becomes dyed, while the liquid, if not too concentrated, finally loses the whole of its colour.

The property of dyeing belongs principally to compounds possessing a more or less marked acid or basic character. It is probable that these properties depend, at least in many cases, on a partly basic, partly acid character inherent in the fibre, which in the one case is developed by the colour-acid and in the other by the colour-base.

The exact relationship between a fibre and a dyestuff is not exactly known. Dyeing processes are usually divided into two categories: adjective, where the use of a mordant is necessary, and substantive, where no third body is required to fix the dyestuff on the fibre.

Two theories as to the nature of substantive dyeing have been advanced, a chemical and a mechanical theory.

The chemical theory of dyeing supposes that a chemical combination of dyestuff and fibre takes place, and this view is, to a certain extent, supported by experimental proof, the researches of Knecht in this direction being especially worthy of attention.

According to the nature of a dyestuff, the fibre may act the part of an acid or of a base: thus dyed fibres are compounds of fibre and dyestuff constituted like salts.

For example, rosaniline is a colourless base, forming red salts. If a skein of wool or silk be warmed in a colourless solution of rosaniline, it becomes dyed red, and as completely as if a corresponding amount of a salt of rosaniline had been employed. This behaviour is easily explained if we assume that the fibre plays the part of an acid, combining with the rosaniline to form a salt which, like rosaniline salts, has a red colour. It may, however, be observed that the red colour of rosaniline salts is only evident in solution, and in the solid state these compounds have a more or less marked bronze-green appearance. This point has been raised by upholders of other theories, that were a salt of rosaniline and fibre formed, it might naturally be expected to possess the green colour of the solid salts of rosaniline.

If we regard dyeing operations as chemical processes, it is probable, in applying salts of colour-bases, that these salts are decomposed in the dyeing process, the fibre combining with the base and the acid being set at liberty. Certain strong basic dyestuffs, such as methyl green, which (like all ammonium bases) forms very stable salts, are not capable of dyeing wool directly. If, however, ammonia is added to the dye-bath, the liberated colour-base combines with the wool and dyes it green. Silk, on the other hand, evidently possesses a stronger acid character than wool, as it may be dyed with methyl green without any assistance. Knecht has demonstrated by quantitative experiments that in dyeing wool with the salts of basic colours, the acid in combination with the colour-base is liberated during the dyeing process. For example, if a solution of rosaniline hydrochloride (magenta) is treated with wool till all colour is extracted, the hydrochloric acid which was in combination with the rosaniline remains in the colourless bath.

The behaviour of some acid dyestuffs also supports the chemical theory of dyeing.

As a rule animal fibres are not capable of decomposing the salts of acid dyestuffs, and in dyeing the colour-acids have to be set at liberty by the addition of a stronger acid to the dye-bath. Certain colour-acids, for example the sulphonic acids of amidoazo-compounds, have a different colour to that of their alkali salts. In dyeing wool with such colour-acids, the shade produced is that of the salts and not that of the colour-acid, so that in such cases wool evidently plays the role of a base.

In certain cases also there is evidence which points to the fact that definite molecular combinations of dyestuff and fibre exist.

In dyeing processes, from a practical standpoint, a certain quantity of dyestuff, seldom exceeding two per cent. of the weight of the fibre, is found necessary to produce a maximum effect as far as shade is concerned. But this by no means expresses the limit to the amount of dyestuff which may be taken up by the fibre, as Knecht has found that wool is capable of extracting far larger quantities from concentrated dye-baths. If a calculation be made based on the amount of picric acid which is taken up by the fibre, it is found that the maximum amounts of naphthol yellow S, tartrazine, and crystal violet which may be combined with wool closely approximate to molecular quantities.

Another conclusion which follows from the researches of the same chemist, is that many cases of so-called substantive dyeing are in reality adjective. In the case of wool, for example, a compound has been isolated, called lanuguinic acid, and it has been found that this acid is capable of entering into combination with dyestuffs, producing compounds which, although amorphous, closely resemble dyed wool in their properties. It is possible that in dyeing wool the action of boiling water liberates this substance, which then effects the combination with the dyestuffs. In this hypothesis, the lanuguinic acid is supposed to be retained in the fibre in a state of solid solution.

A theory of solid solution has been applied in a somewhat different form by Witt to the substantive dyeing of wool, silk, and cotton. A skein of silk dyed with magenta is according to the chemical theory a combination of magenta and silk, and it requires pretty strong soaping to remove the dye. But if the silk be treated with alcohol, which is certainly capable of exerting only a solvent effect, all the colouring-matter is quickly removed. If water is added to the alcoholic solution, the dyestuff, however, returns to the silk. This behaviour, unexplained by the chemical theory of dyeing, may be cleared up by the "solid solution" theory. In this especial instance of silk and magenta, we must suppose that the essential constituent of the silk fibre, fibroin, has a greater solvent action for magenta than water, and thus withdraws it from its aqueous solution. Alcohol having a greater solvent power than the fibroin, removes the dyestuff from the fibre. Similar cases are frequent in purely chemical operations, and the extraction of magenta from its aqueous solution by silk is exactly similar to the removal of resorcin from an aqueous solution by ether.

The different behaviour of various textile fibres in dyeing may be explained by an assumption of different solvent power; thus, silk dyes more readily than other fibres because the fibroin has a greater solvent power. Keratine again, the principle of the wool fibre, possesses a greater solvent power than cellulose, which is only capable of attracting and holding in solution a few dyestuffs, such as the tetrazo-dyes of the benzidine series, and in certain cases in this class the solvent power of the water in the dye-bath has to be decreased by addition of salt.

The mechanical theory of dyeing is based on the assumption that the molecules of colouring-matter leave the dye-bath and are mechanically deposited between the molecules of the fibre.

Certain plant-fibres—for example jute, the bast-fibre of *Cor-*

chorus—have the property of fixing dyestuffs directly, this being due to the presence of an incrustation of foreign matter, present on the fibre.

Many amorphous substances, amongst which may be mentioned precipitated sulphur, gelatinous silica, and Kieselguhr, have the power of attracting basic dyestuffs.

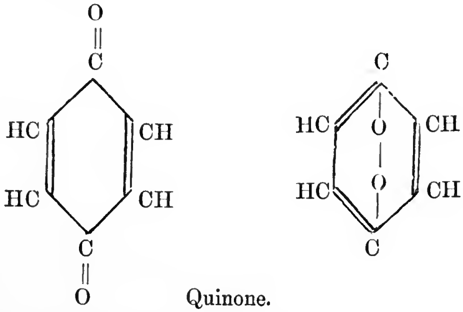
The properties of the so-called oxycellulose are also of interest from a tinctorial standpoint. On oxidation of vegetable fibre (cellulose) with chlorine, chromic acid, or similar agents, it undergoes a change, and becomes capable of fixing basic dyestuffs without a mordant.

A consideration of the radicals capable of acting as chromophors shows that only two of these, the nitro- and nitroso-groups, are monatomic. If these groups are introduced alone into a hydrocarbon, the body produced possesses scarcely any colour. A coloured body is formed if a salt-forming group be also introduced, the latter probably forming a closed ring with the chromophor. The case is similar when a valent chromophor is introduced into several hydrocarbons, so that each valency is attached to a hydrocarbon group not in linkage with any other. This is the case with the ketones, while the diketones (quinones) and simple ketones possessing a ring constitution (diphenylene ketone) are coloured compounds.

Azobenzene forms an apparent exception to this rule (see below).

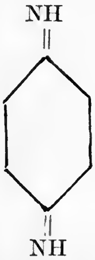
The ketone group, especially when it occurs twice, as in the quinones, is one of the most important chromophors. The oxygen atom of the ketone group may be replaced by another diatomic radical, such as sulphur; or the ketone carbon atom may enter into combination with two valencies of a diatomic nitrogen atom: the resulting groups $C{=}S$ and $C{=}N$ in general possess increased chromophoric properties. As an example of this, it may be remarked that the derivatives of simple ketones are colourless, those of the thioketones, ketone-imides, and hydrazides being coloured.

The ketone group $C{=}O$ appears only to act as a chromophor when it occurs as a member of a closed ring of carbon atoms. A large number of dyestuffs may be regarded as built up similarly to the di-ketones (ortho- and para-quinones); and as the present view of the constitution of the quinones is expressed by the following formula, the formulæ of a large number of dyestuffs have to be modified accordingly.

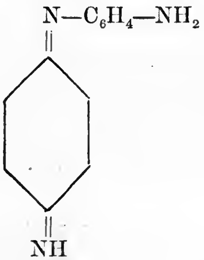


Quinone.

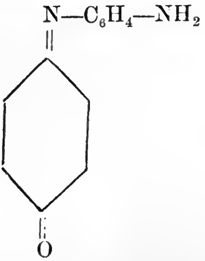
The indamines are derivatives of quinone-imide, and accordingly a change from a tertiary to a secondary carbon atom must be accepted in the constitutional formulæ of these bodies.



Quinone-imide (unknown).

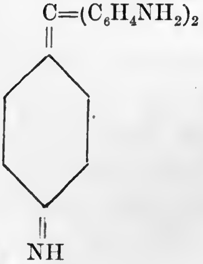


Indamine.

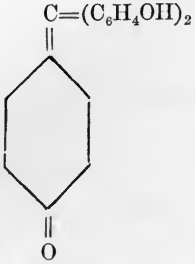


Indophenol.

A similar constitution may be accepted for rosaniline and rosolic acid.



Rosaniline.



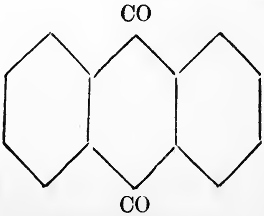
Rosolic acid.

In these cases the oxygen of the ketone group is replaced by a diatomic methane rest.

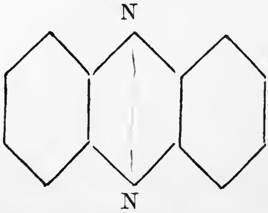
A class of bodies closely resembling the paraquinones are the orthoquinones, for example β-naphthaquinone and phenanthrenequinone are members of this class of compounds. From these a new class of compounds may be obtained, and these bodies, the azines, are in some respects analogous to the paraquinones.

If an orthodiamine interacts with an orthoquinone, the oxygen atoms of the latter are eliminated, and tertiary nitrogen atoms enter in their places, a new ring containing two nitrogen atoms and four carbon atoms being formed. The similarity of this ring to the paraquinone ring exists in the fact that in the former tertiary nitrogen atoms take the place of the chromophoric C═O groups of the latter.

This analogy is especially marked if the constitutional formula of anthraquinone is compared with that of the simplest aromatic azine.



Anthraquinone.



Phenazine.

There are also certain points of resemblance between the azines and quinoline and acridine: here only one carbon atom is replaced by nitrogen, and it is probably owing to this that the chromogenic nature of these bodies is not so strongly marked as that of the azines.

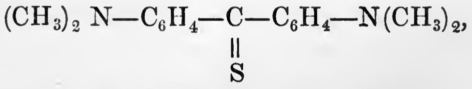
Generally speaking, the introduction of the simplest chromophors gives rise to yellow dyestuffs, and when stronger and more complex groups are introduced the colour changes through red to blue &c. For example, all quinoline and acridine dyestuffs are yellow, while only the simplest azines have this colour and become red and blue by introduction of salt-forming groups.

In some other dyestuffs the presence of the lactone ring C=O—O— is assumed, and here again the oxygen atom may be replaced by a primary nitrogen atom (indigo dyestuffs).

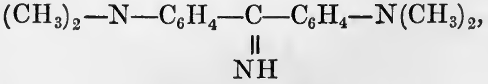
It will be noticed, on examining the constitution of the chromogens already treated of, that most of them contain the chromophor as member of a closed ring, differing from the other members in valency and linkage.

For instance, compounds constituted on the quinone type contain two secondary and four tertiary carbon atoms. In cases where four secondary carbon atoms are present, as in rhodizonic acid, $C_6(OH)_2O_4$, the body is still coloured; but if all the six carbon atoms of benzene become secondary, as in triquinoyl or perquinone, C_6O_6, the colour disappears *. The same occurs if all the carbon atoms of quinone become tertiary, *i. e.* by reduction of the quinone to hydroquinone.

An attempt to explain the colours of all carbon compounds by the existence of such rings possesses great interest, but it cannot be denied that the necessary conditions are absent in numerous dyestuffs, for example, thioketones, ketone-imides, and hydrazides are such bodies, *i. e.* tetramethyldiamidothiobenzophenone and auramine,



$$(CH_3)_2\ N—C_6H_4—\underset{\underset{S}{\|}}{C}—C_6H_4—N(CH_3)_2,$$



$$(CH_3)_2—N—C_6H_4—\underset{\underset{NH}{\|}}{C}—C_6H_4—N(CH_3)_2,$$

in which the chromophors CS and CNH are not present as a ring but as an open chain.

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* The researches of Hantsch (Ber. xx.) make it improbable that the absence of colour in triquinoyl and leuconic acid is due to hydration.

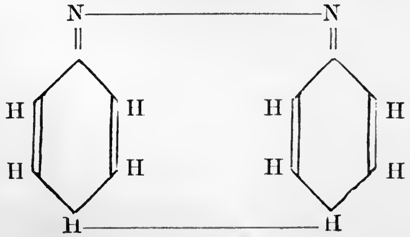
The nitro-compounds, which are almost the only class in which a monatomic group acts as chromophor, would also be difficult to bring under the above ring classification. There is no doubt, however, that in amido- and hydroxyl derivatives of nitro-bodies there is a certain relationship between the nitro-group and the hydroxyl or amido-group. It is not improbable that the nitrophenols possess a similar constitution to the nitrosophenols, which are now generally regarded as quinoneoximes. The azo-dye-stuffs are a class of bodies the properties of which are not in accordance with their constitution, and this is especially marked in the first member of the series, azobenzene.

If a single hydrogen atom in a benzene ring is substituted, or if two rings are joined together by a diatomic radical, the bodies formed are colourless or only slightly coloured, while azobenzene is an intensely coloured compound and a powerful chromogen.

This leads to the supposition that azobenzene does not act according to the simple constitutional formula $C_6H_5N{=}NC_6H_5$ in certain cases, and other facts tend to speculation as to a more complex formula.

Azobenzene and its derivative hydrazobenzene may be converted into a derivative of diphenyl, benzidine; and the ease with which this reaction takes place seems to point to the existence of an unstable linkage between the benzene rings. This would be most readily explained by the assumption that a change in the linkage (from double to single) between the carbon atoms in the benzene chain takes place in a similar manner to the linkage in the quinone formula.

The following formula would then express the constitution of azobenzene :—



Naturally such formulæ are hypothetical, and only of interest in attempting to regard all dyestuffs as variations of a common system.

A characteristic of the radicals which act as chromophors is that they are never perfectly neutral groups, or in other words their introduction confers a certain tendency towards basic or acid properties to the bodies which they enter.

By introduction of salt-forming groups these properties become strengthened in one or other of these directions. According to their nature, therefore, these chromophors may be classified as basic or acid-forming. The quinone group, for example, possesses strong acid-forming properties. A simple hydroxyl derivative of a hydrocarbon possesses weak acid properties, while the hydroxyl derivatives of the quinones have these properties in a far higher degree. The nitro-group acts similarly. Chromophors which contain nitrogen without oxygen tend to form bases.

We have still to consider more closely the nature of the salt-forming groups which have already been mentioned.

These groups may act totally differently, and are divided into two sharply defined classes.

Certain radicals, generally acid, such as the sulpho-group, SO_3H, and the carboxyl group, if introduced into a chromogen, confer upon it acid properties, but without increasing the colour appreciably, indeed in many cases the dyeing power is considerably decreased.

Such bodies act as acid dyestuffs, and the group introduced effects the combination with the fibre.

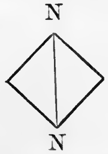
Azobenzene, for example, has no affinity for animal fibres, being perfectly neutral, while its sulphonic and carbonic acids act as weak dyestuffs. The influence of amido- and hydroxyl groups is a totally different one.

By introduction of these radicals the chromogen acquires basic or acid properties, and at the same time a considerable modification in the colour of the body is produced. The colour generally becomes more intense; in many cases colour is only produced when these groups enter. Having regard to these facts the groups (sulpho- and carboxyl) may be termed "salt-forming," while for the latter Witt has recently suggested the name auxochromic (Ber. xxi. p. 325).

The relationship existing between these groups and the chromophors is not yet explained. In the case of the oxyquinones it has already been pointed out that the chromophoric quinone group confers strong acid properties on the auxochromic hydroxyl group. The same is also observed in the phthaleïns and rosolic-acid dyestuffs. These hydroxyl groups play at the same time the part of salt-formers, and produce the necessary affinity for the fibre. The auxochromic amido-groups exert a somewhat different influence on the base-forming amido-groups. This behaviour may easily be explained by studying the basic triphenylmethane dyestuffs, for instance rosaniline. Rosaniline contains, besides the chromophor $=C=R=NH$, two auxochromic amido-groups.

It is certain that the imide group of this chromophor combines with the acid in the formation of the red monoacid rosaniline salts, and it is by its means that the combination with the fibre is effected. The latter is deduced from the fact that rosaniline dyes the colour of these salts, while the salts formed by neutralising the two amido-groups are yellow.

The amidoazines show this characteristic in a somewhat more striking manner. The azines contain the chromophor :—



and the simplest members of the series are weak bases forming salts which are mostly red or violet and only stable in presence of an excess of acid.

The amidoazines, for example toluylene red (diamidoazine), are strong bases forming red monoacid salts, which, however, are stable.

Here also the acid radical is combined with the azine group, and the amido-groups only form salts in presence of an excess of acid, the change being accompanied by a characteristic change of colour through blue to green.

In dyeing, toluylene red produces a red shade, and not a blue or green, so that the azine group alone enters into combination with the fibre.

It is easily seen that in these cases the auxochromic amido-groups tend to strengthen the basic character of the chromophor, but do not act as salt-formers. At the same time the colour becomes more intense. According to a rule which has been laid down by Witt, the stronger of two similar dyestuffs is always that which possesses salt-forming properties in a higher degree.

From this it may be conceived that the simultaneous presence of a basic auxochromic group and an acid-forming chromophor, or *vice versa*, gives rise to a weak dyestuff. The nitranilines form a case in point; they are weak dyestuffs, while on the other hand the nitrophenols have tinctorial properties much more fully developed.

From the foregoing reasons actual dyestuffs are divided into two principal classes—acid and basic.

Certain coloured bodies like indigo are neutral, and possess no affinity for textile fibres. Their dyeing is effected by precipitating on the fibre from a solution as in vat dyeing, or by converting into a sulphonic acid, and thereby producing a capability to form salts.

The salts of certain azosulphonic acids may be termed neutral dyestuffs. They may be directly fixed on vegetable fibres.

Most basic and acid dyestuffs are fixed without aid by animal fibres; vegetable fibres, on the other hand, require the intervention of a special mordant. Tannic acid is generally used along with basic dyestuffs, as it forms insoluble salts with these compounds.

Cotton possesses the power of attracting a certain amount of tannic acid from solutions containing this body, and of retaining it even after washing. Cotton prepared in this manner may be dyed with most basic dyestuffs just as well as wool. In practice the cotton treated with tannic acid is further submitted to the action of tartar emetic or some other antimony compound. An insoluble salt of tannic acid and antimony oxide is formed, and this fixes basic dyestuffs with the greatest ease. The advantage of the latter method is that the shades produced are faster to soap. Some acid dyestuffs combine with metallic oxides, producing insoluble lakes, different in colour to the original dyestuffs, and varying considerably with the metallic oxide used. This property is much used to effect the fixation of dyestuffs on the fibre, especially on cotton. Anthraquinone derivatives are always fixed in this manner, and numerous natural dyestuffs also.

This peculiar property of dyeing on metallic mordants has as yet had no satisfactory explanation. If cotton mordanted with alumina or oxide of iron is placed in an alizarin bath, the lake is precipitated and enters into intimate combination with the fibre.

Many dyestuffs form insoluble lakes with metallic oxides, but the property of combining with mordants on the fibre is peculiar to a few. Insoluble lakes may be obtained from the eosines and from all oxyanthraquinones, but the former class of bodies cannot be fixed on mordants, and of the latter only derivatives of alizarin possess this property.

It is necessary that the lake produced forms a certain combination with the fibre; if not, it is only retained superficially, and is removed mechanically during the dyeing process. It has been found that this capability of dyeing on mordants stands in close relationship to the constitution of the colouring-matter, and more especially to the relative positions of the substituting groups (compare quinone dyestuffs).

The commercial value of a colouring-matter is best determined by dye-trial; in fact this is the only trustworthy method, and the numerous processes which have been proposed to determine dyestuffs volumetrically are untrustworthy, as they are readily influenced by the nature of the impurities present.

Exceptions may be made in dealing with a few dyestuffs which come into commerce in a pure state.

For instance, alizarin is tested by a dye-trial, and then examined after washing carefully for the amount of solid matter and ash which it contains.

The testing of colouring-matters by means of dye-trials is simply colorimetric comparison of a dyestuff with a standard of known quality. If equal quantities of two samples of a dye are dyed upon equal weights of wool or silk, a difference of two to five per cent. may be distinguished from the difference in shade observed in the two patterns.

By a second dyeing it is easy to determine the difference between the quantities of the two dyestuffs required to produce the same shade, and a simple calculation then gives the value of the product tested, compared with the standard. At the same time an idea is obtained of the relative purity of the shade of the dyestuffs and of the nature of the impurities which may be present.

In printing, both basic dyestuffs and acid ones capable of forming lakes with metallic oxides are employed.

The principle of the fixation of basic dyestuffs in printing depends on the insolubility of the tannin compounds.

The tannates of all colour-bases are insoluble in water, but mostly dissolve in dilute acetic acid. The dyestuff is printed along with tannin and dilute acetic acid. The acetic-acid solution of the tannin lake penetrates the fibre, and subsequent steaming removes acetic acid, leaving an insoluble lake on the fibre. The shades may be made faster to soap by passing through tartar emetic.

Acid dyestuffs, like alizarin &c., are printed in the free state along with the metallic mordants (aluminium, iron, or chromium acetate); on steaming, acetic acid is driven off and the metallic oxide combines with the colour-acid to a firmly adhering lake.

Only a few natural dyestuffs (indigo, alizarin, and purpurin) have been prepared synthetically, but the number of artificial dyestuffs is very large. Some of these, especially the phthaleïns and rosolic acid, seem to approach the natural dyestuffs in constitution, but the greater number belong to special classes, which are without analogue in either the animal or the vegetable kingdom.

Natural dyestuffs, with few exceptions (indigo, berberine), contain only carbon, hydrogen, and oxygen; while many classes of artificial colouring-matters contain nitrogenous groups, often of a decided basic nature. Some others again contain chlorine, bromine, iodine, or sulphur. The raw materials for the preparation of these bodies are, at the present time, almost exclusively products of dry distillation, and the most important of these is coal-tar, obtained as a bye-product in the manufacture of illuminating-gas. The discovery and first preparation of artificial dyestuffs is therefore closely associated with the earliest studies on products of dry distillation; and the development of the gas industry has, hand in hand with a series of scientific researches appertaining thereto, brought the important colour-manufacturing industry into existence.

The honour of preparing the first colouring-matters from products of dry distillation belongs to von Reichenbach (pittacal from wood-tar, 1832), and to Runge (rosolic acid from coal-tar, 1834) [1].

For a long time, however, the discoveries of these chemists remained in obscurity, and it was only after the knowledge of products of dry distillation had been considerably advanced by later researches, that the production of coloured derivatives again attracted the interest of chemists.

Hofmann, Zinin, and Fritsche were the first to show the relationship between benzene, aniline, phenol, &c.; and the first explanation of the constitution of these products formed the foundation of the colour-industry.

The first dyestuff prepared and applied on an industrial scale was "mauve," introduced by Perkin in 1856. About the same period the formation of rosaniline was noticed by Nathanson, who obtained it by heating aniline with ethylene chloride [2].

Two years later Hofmann [3] announced the discovery of a red product, obtained by the action of carbon tetrachloride on aniline. Hofmann and Nathanson, if their experiments were made with pure aniline, must have already had pararosaniline in their hands.

The next ten years were almost entirely devoted to the scientific study and technical development of rosaniline and its derivatives.

The first patent was taken out by Renard frères and Franc, of Lyons, on April 8th, 1859 [4], for the preparation of a red dyestuff, according to a process discovered by Verguin, which consisted in the action of stannic chloride on aniline.

Numerous patents followed in England and France, depending on the action of other oxidising agents than stannic chloride. In some of these patents, however, it is not clear whether rosaniline or some other dyestuff such as mauve is really produced. Renard frères introduced their products, still very impure, under the name "fuchsine."

The process of Gerber-Keller with nitrate of mercury is the only one of any value (October, 1859) [5].

In the following year, 1860, the application of arsenic acid as oxidising agent was patented by Medlock and by Nicholson almost simultaneously in England [6]. A few months later the same process was made the subject of a French patent by Girard and De Laire [7].

In 1861 Laurent and Castelhaz [8] patented the action of nitrobenzene on iron and hydrochloric acid, and this is evidently the first opening of the nitrobenzene process. In the same year the synthesis of rosolic acid was effected by Kolbe and Schmitt [9].

The formation of aniline blue was also first observed in 1861 by Girard and De Laire; and in the following year the process was further developed by Nicholson [10], by Monnet and Dury [11], who used acetic acid in the manufacture, and by Wanklyn [12], who applied benzoic acid.

In 1862 the composition of rosaniline, and its formation from aniline and toluidine, was further explained by A. W. Hofmann [13].

Aldehyde green was also discovered in 1862 [14].

In 1863 the same chemist prepared ethyl- and methyl-derivatives of rosaniline, and showed aniline blue to be triphenylrosaniline [13].

Aniline black was first prepared in 1863 by Lightfoot [15].

The first azo-dyestuffs were introduced between 1864 and 1866. Amidoazobenzene [16] appeared first, and was quickly followed by phenylene brown [17].

Caro and Wanklyn [18] demonstrated the relationship between rosaniline and rosolic acid in 1866; and in the same year Keisser took the first patent for iodine green [19].

Diphenylamine blue was prepared by Girard and De Laire in 1867 [20].

In the same year methyl violet, which had already been noticed by Lauth in 1861, was manufactured on a large scale by Poirrier and Chapat.

The composition of iodine green was determined by Hofmann and Girard in 1869 [21]; and Rosenstiehl demonstrated the existence of several rosanilines [22].

The synthesis of alizarin was carried out by Graebe and Liebermann [23] in the same year, this being of very great importance, as the first synthesis capable of industrial application for production of a dyestuff occurring in nature.

In 1872 Hofmann and Geyger [24] examined induline and saffranine, the latter a dyestuff which had appeared in commerce a few years previously.

In 1873 Hofmann published his researches on methyl violet and methyl green [25].

In 1874 the phthaleïns (eosine), discovered by Bayer and Caro, were introduced into commerce.

In 1876 pararosaniline was discovered by E. and O. Fischer, and the relation of this body to triphenylmethane demonstrated [26].

In 1877 Prud'homme discovered alizarin blue; its industrial production was effected by Brunck in the following year.

In the same year Caro [27] produced methylene blue, basing his process on the sulphuretted hydrogen reaction observed by Lauth in 1876 [28]. Almost simultaneously malachite green was discovered by E. and O. Fischer [29] and by Doebner [30]; and O. N. Witt and Roussin introduced the synthesis of azo-dyes on a manufacturing scale, which proved afterwards to be of such great importance.

In 1880 Bayer took out the first patent for the production of artificial indigo [31].

In 1881 this was followed by indophenol [32] and the gallocyanine of Witt and Koechlin.

In 1883–84 Caro and Kern [33] effected the synthesis of triphenylmethane dyestuffs by means of carbon oxychloride, and this was applied to the production of auramine and Victoria blue.

The constitution of numerous dyestuffs has been determined by purely scientific researches, and these have been of great service in discovering new synthetical methods, many of which are applied on a large scale.

In 1886 an important development took place in the azo colour-industry. This was based on an observation made by Griess (pat. 1884), that certain azo-dyestuffs derived from benzidine were capable of dyeing vegetable fibres without mordant. As members of this class of dyestuffs, which are very numerous, may be mentioned chrysamine, congo red, benzo-purpurine, &c.

In 1888 Witt explained the constitution of the saffranines by his classic researches on the azines; and not long afterwards, Fischer and Hepp proved that the indulines were also derivatives of azines.

The rhodamines, a class of dyestuffs allied to the phthaleïns, were introduced in 1888.

The present requirements of the colour-industry as raw materials are benzene and its homologues (toluene and xylene), naphthalene, and anthracene, obtained from coal-tar. The coal-tar of the gas-works is first worked up in tar-distilleries, the above bodies being obtained in a more or less impure state. The further purification is carried on in some colour-works; but this generally takes place in intermediate manufactories where the crude products are purified and worked up into a higher stage, benzene and its homologues being made into aniline, toluidine, and xylidine, and naphthalene into naphthylamine. The crude benzol is first submitted to a careful fractional distillation, and benzene, toluene, and xylene are separated in as pure a state as possible. The hydrocarbons boiling at a higher temperature find their principal application for solvent purposes, hence they are principally met with under the designation "solvent naphtha." One purpose for which it serves is the purification of anthracene. Benzene, toluene, and xylene are converted into aniline, toluidine, and xylidine by nitration and subsequent reduction.

These bases are at present prepared by aniline-works in a state of great purity; for instance the aniline employed in the manufacture of blue ("blue oil") is required to be chemically pure.

The "red oil" used in the manufacture of rosaniline is a mixture containing aniline, ortho- and para-toluidine in varying proportions.

A classification of the organic dyestuffs from a chemical standpoint is in many respects a subject of great difficulty. Most text-books have adopted a division in which the dyestuffs are classified according to the hydrocarbon from which they are derived; this, however, is far from natural, as by its means some groups which are chemically well characterized, such as the azo-dyes, are divided; and, on the other hand, dyestuffs of totally different constitution are placed together.

In the following classification an attempt is made to group the colouring-matters according to their chemical constitution, especial regard being paid to their colour-giving groups. In many cases this is rendered difficult, however, by the somewhat scanty knowledge of the relations existing between constitution and dyestuff character.

The final class, "Dyestuffs of unknown constitution," is still a very numerous one.

This group comprises most natural dyestuffs: the constitution of some of these (alizarin and indigo) is known, and admits of systematic classification with just as much justice as the purely artificial dyestuffs; and it would be reasonable to treat of the whole in a single chapter of natural dyestuffs.

It must not be conceived that the constitution of all the colouring-matters here classified is completely explained, in many cases it is deduced from analogy in formation to that of bodies of known constitution; but as to the constitution of dyestuffs which have not been prepared synthetically, we are altogether without knowledge.

The organic colouring-matters may be grouped as follows :—

I. Nitro-Compounds.
II. Azo-Compounds.
III. Oxyquinones and Quinoneoximes.
IV. Ketone-imides and Hydrazides.
V. Triphenylmethane Derivatives.
VI. Quinone-imide Dyestuffs.
VII. Azine Dyestuffs.
VIII. Aniline Black.
IX. Indulines and Nigrosines.
X. Quinoline and Acridine Dyestuffs.
XI. Indigo Dyestuffs.
XII. Euxanthic Acid and Galloflavine.
XIII. Canarine.
XIV. Murexide.
XV. Dyestuffs of unknown constitution.

CHEMISTRY

OF THE

ORGANIC DYESTUFFS.

CHAPTER I.

NITRO-COMPOUNDS.

THE nitro-derivatives of amines and phenols are dyestuffs, of a more or less pronounced character. The phenol derivatives have the greater tinctorial power, as the nitro-group is a chromophor which confers acid properties, and therefore possesses the power of decreasing the basic properties of the amido-group. Indeed, in the case of certain bodies of only feebly basic properties, the introduction of several nitro-groups may produce an acid dyestuff, for example, diphenylamine is a body of this class.

Acid nitro-compounds are especially strongly coloured in the form of salts; paranitrophenol, for example, is a colourless body, yielding yellow salts. On the other hand, basic nitro-compounds form colourless salts with acids.

The compounds produced when the acid properties of the hydroxyl group are removed by introduction of an alcohol radical are colourless, for instance, nitroanisol behaves like a nitro-derivative of a hydrocarbon.

Those nitrophenols which contain the nitro-group and the hydroxyl group in the ortho position to each other, are as a rule the most strongly coloured.

The close relationship existing between the nitrophenols and the nitrosophenols, and the assumption generally accepted, that the latter are quinoneoximes, render it probable that a similar structure may be ascribed to the nitrophenols, and that in the latter there is a certain connection between the nitro and hydroxyl groups.

The number of coloured nitro-compounds is very large, and in the present place it is impossible to consider more than those which possess technical interest. They are all acid dyestuffs; since the introduction of the azo-dyestuffs their application has become considerably less.

Trinitrophenol (Picric Acid) [1, 2, 3].

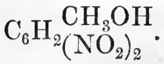
$C_6H_2(NO_2)_3OH$.

Picric acid is formed by the action of nitric acid on phenol, and on many other organic bodies (indigo, xanthorrhœa resin, aloes, &c.). On a large scale it is obtained by the action of concentrated nitric acid on phenol-sulphonic acid [2].

In a pure state picric acid forms light yellow leaflets, M.P. 122°·5 C. It dissolves somewhat sparingly in water, more easily in alcohol.

It forms well crystallized salts with metallic oxides; the potassium salt, $C_6H_2(NO_2)_3OK$, is difficultly soluble. Picric acid dyes wool and silk from an acid bath, a fine greenish shade of yellow being produced. Although this shade is not fast, it finds considerable application in silk-dyeing, and serves principally for production of compound colours, especially for modifying green and red dyestuffs.

Dinitrocresol.



$$C_6H_2\begin{matrix}CH_3OH\\(NO_2)_2\end{matrix}.$$

The sodium salt of a dinitrocresol formerly came into commerce under the name "Victoria Yellow" or Saffron substitute [5].

It was probably obtained by treating crude creosol with nitric acid, partly also by diazotising crude toluidine and boiling the resulting compounds with nitric acid. It consists chiefly of a mixture of dinitroparacresol ($CH_3 : OH : NO_2 : NO_2 = 1 . 4 . 3 . 5$), M.P. 83°·5, and dinitro-orthocresol (1 . 2 . 3 . 5), M.P. 85°·8 [4]. It is now, however, almost out of the market.

Dinitronaphthol (MARTIUS YELLOW).

$$C_{10}H_5(NO_2)_2\overset{a}{O}H.$$

Dinitro-*a*-naphthol was formerly obtained by boiling *a*-diazonaphthalene [6] with dilute nitric acid; at the present time it is manufactured by the action of nitric acid on *a*-naphthol sulphonic acid (mono- or di-sulphonic acid) [7].

Pure dinitronaphthol forms needles, which are sparingly soluble in water and difficultly soluble in alcohol, ether, or benzene. It melts at 138°, and forms salts which are moderately soluble in water.

The commercial product is generally the sodium salt, though the lime salt is occasionally met with. It dyes wool and silk in an acid bath, a fine golden-yellow shade being obtained. The principal drawback in the use of this dyestuff is that it is volatile at a comparatively low temperature, and is therefore liable to mark off.

Another application of dinitronaphthol is for colouring confectionery, as it does not possess the bitter taste peculiar to most nitro-compounds.

Dinitronaphthol Sulphonic Acid (NAPHTHOL YELLOW S.)

$$C_{10}H_4(NO_2)_2\overset{a}{O}H\ HSO_3.$$

By the action of nitric acid on *a*-naphthol mono- and di-sulphonic acids (obtained by direct sulphonation), the sulpho-groups are replaced by nitro-groups, while on nitration of *a*-naphthol trisulphonic acid, one sulpho-group remains intact [8], the other two being replaced by nitro-groups. The compound formed is a monosulphonic acid of dinitronaphthol. This acid forms long yellow needles, which are easily soluble in water [9].

The commercial product consists of the potassium salt, which is sparingly soluble. On wool and silk it dyes the same shades as Martius yellow, but is to be preferred as yielding much faster dyes.

It may be distinguished from Martius yellow by treating its solution with acids; Martius yellow is immediately precipitated, while naphthol yellow S gives no reaction.

Brilliant Yellow.

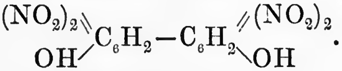
This dyestuff is prepared by the nitration of the *a*-naphthol disulphonic acid of the Schollkopf Co. It is an isomer of naphthol yellow S, but little is known of its dyeing properties.

Tetranitronaphthol [10].

$$C_{10}H_3(NO_2)_4\overset{a}{O}H.$$

Tetranitro-*a*-naphthol is obtained from tetranitrobromnaphthalene by treating with an alkali. It forms yellow needles which melt at 180°. It gives fine orange shades on wool and silk, but it is not fast to light, and has only obtained slight appreciation under the designation "Sun gold."

Tetranitrodiphenol.



$$\begin{matrix}(NO_2)_2\diagdown \\ OH\diagup\end{matrix}C_6H_2-C_6H_2\begin{matrix}\diagup\!\!\diagup(NO_2)_2 \\ \diagdown OH\end{matrix}.$$

This colouring-matter formerly came into commerce in form of its ammonium salt as "Palatine orange," and was used in paper-dyeing. It is formed by treating benzidine with nitrous acid, and boiling the resulting tetrazodiphenyl with nitric acid.

Hexanitrodiphenylamine (AURANTIA) [11].

$$(NO_2)_3C_6H_2NHC_6H_2(NO_2)_3.$$

Hexanitrodiphenylamine is produced by energetic action of nitric acid on diphenylamine. It forms yellow prisms, M.P. 238°, and behaves like an acid, forming stable crystalline salts with the alkalies. It dyes an orange shade on silk and wool, but since the introduction of the azo-dyes is scarcely ever used.

Salicyl Yellow (NITROBROMSALICYLIC ACID) [13].

The nitro-compounds which are formed by treating monobromsalicylic acid with nitric acid have been tried experimentally in dyeing. They are very fugitive to light, and this, together with their high price, renders them unsuitable for technical application.

Mononitrobromsalicylic acid dyes a very pure yellow on wool and silk from an acid bath, the dinitro-compound yields a more orange shade.

Isopurpuric Acid.

$C_8H_5N_5O_6$.

The potassium salt of this acid, which is also known as picrocyaminic acid, is obtained by treating picric acid with solution of potassium cyanide. The ammonium salt obtained from the potassium salt by double decomposition with ammonium chloride was formerly used in dyeing under the name "Grenat soluble." It produces reddish-brown shades on wool and silk, but has now entirely disappeared.

Another colouring-matter which formerly occurred in commerce is picramic acid, $C_6H_2(NO_2)_2NH_2OH$, obtained from picric acid by partial reduction.

CHAPTER II.

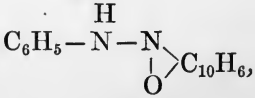
AZO-COMPOUNDS.

THE Azo-dyestuffs form a well-characterized group of compounds containing the azo-chain —N=N— as chromophor.

This divalent group is always linked with two benzene rings or other aromatic hydrocarbon, and thus differs from the diazo-group, which is similarly constituted in other respects. The introduction of the azo-group into hydrocarbons or bodies acting similarly (anisol, phenetol) gives rise to the formati[illegible]of coloured compounds, which, however, are not dyestuffs. [illegible]e affinity for fibres is only acquired when groups are introduced which confer acid or basic properties to the azo-compounds.

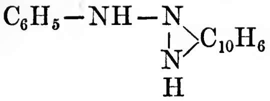
Azobenzene, though intensely coloured, is not a dyestuff. Azobenzene-sulphonic acid possesses tinctorial [illegible]rope[illegible], although only to a slight extent; but if auxochromic group[illegible], such as the amido or hydroxyl groups, are present, the dyeing power is considerably increased, and at the same time the shade is considerably modified. It is probable that in this class of compounds there exists a certain linkage between the auxochromic and the chromogenic groups, this linkage being easily dissolved under certain circumstances.

Liebermann deduced the following formula for β-naphthol-azobenzene [1],



$$C_6H_5-\overset{H}{N}-N\underset{O}{\overset{\diagdown}{|}}\!\!\!>C_{10}H_6,$$

from the fact that this body does not act as a phenol. In a similar manner Zincke ascribes one of the following formulæ to the compound produced by the interaction of diazobenzene and β-naphthylamine [2] :—



$$C_6H_5-NH-\begin{matrix}N\\|\\N\\H\end{matrix}>C_{10}H_6$$

or

$$C_6H_5-N<\begin{matrix}NH\\NH\end{matrix}>C_{10}H_6.$$

It cannot be denied that many reactions of oxy- and amidoazo-compounds, especially those of the ortho series, are easily explained on the assumption that these formulæ are correct; but, on the other hand, amidoazo-compounds are capable of reacting as true amines.

The above formulæ show a certain analogy to the quinones, especially marked, if written slightly differently,

$$C_6H_5-NH-N=C_{10}H_6=O \quad \text{and} \quad C_6H_5-NH-N=C_{10}H_6=NH.$$

An important support for this theory is the circumstance that the bodies formed by the action of aromatic hydrazines on quinones are identical with those obtained from phenols and diazo-compounds. Phenylhydrazine, for example, reacts with α-naphthoquinone, producing the same compound which is formed by combination of α-naphthol with diazobenzene [3]. The first method of formation renders the formula

$$C_6H_5-NH-N=C_{10}H_6=O$$

probable, while the latter affords just as good reason for the formula

$$C_6H_5-N=N-C_{10}H_6-OH.$$

The compounds from hydrazines and ketones or quinones (hydrazides) are so closely related to the azo-series, that one is almost compelled to place them under the same classification.

The property of forming combinations with sodium bisulphite is common alike to azo-dyes, ketones, and quinones [4]. A difference in the constitution of ortho- and para-derivatives cannot well be accepted, as the same reactions may be obtained with each, though with varying degrees of ease.

As has already been stated, the azo-compounds react like amido- or hydroxyl compounds in certain cases; for example, all amido-azo-compounds yield diazo-compounds. It is possible that two forms exist in such cases, and that these react in one way or another according to circumstances.

The older constitutional formulæ have been used in the following pages, this being the general method, and as there is just as much evidence in favour of the old formulæ as there is for the new. The simplest azo-compounds, like dyestuffs of simple constitution, have in general a yellow colour. By increasing the number of auxochromic groups, or by building-up of carbon atoms in the molecule, the shade becomes deeper. In many cases it goes through red to violet, in others it becomes brown. Blue dyestuffs of this class have only been obtained by introduction of several azo-groups in the molecule (dis- or tetrazo-dyestuffs).

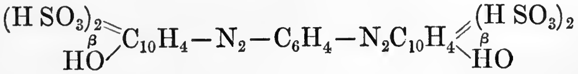
Azo-dyestuffs of a green colour have not yet been obtained, although many form green compounds with acids.

The so-called "azo-green," although containing an azo-group, owes its colour to the rest of triphenylmethane present.

Dyestuffs which contain benzene and no higher hydrocarbon are mostly yellow, orange-yellow, or brown. By the introduction of a naphthalene group, red colouring-matters are formed, and blue and violet dyestuffs are obtained if the naphthalene ring occurs several times.

The introduction of a radical of totally indifferent properties (as the methoxyl group, —O CH_3) may produce a great alteration in the colour of the compound operated upon.

The relative positions of the chromophor groups have also a decided influence in this direction. The compound



$$\begin{matrix}(H\,SO_3)_2 \\ \overset{\beta}{HO}\end{matrix}\!\!>C_{10}H_4-N_2-C_6H_4-N_2C_{10}H_4<\!\!\begin{matrix}(H\,SO_3)_2 \\ \overset{\beta}{HO}\end{matrix}$$

is blue if the azo-groups are in the para-position in the benzene ring, and red if in the meta-position.

The general rule that the depth of colour of a compound increases with the number of atoms constituting the molecule, does not apply in all cases; for example, the above dyestuff is redder, if the connecting benzene ring is replaced by a higher hydrocarbon.

Nearly all azo-dyestuffs give characteristic colour-reactions on dissolving in strong sulphuric acid, and it is probable that in such cases the basic properties of the azo-group become apparent by the action of the strong acid. It is worthy of notice that most substituted azo-dyes give the same reaction with sulphuric acid as the azo-hydrocarbon from which they are derived. Azobenzene dissolves in sulphuric acid with a yellowish-brown colour; and the same colour is obtained with its oxy- and amido-derivatives, although the latter are coloured red by dilute acid. *α*-azo-naphthalene, and its oxy- and amido-derivatives, give a blue coloration with concentrated sulphuric acid. In mixed azo-compounds the presence of a sulpho-group may produce interesting changes according to its position. *β*-naphthol-azobenzene, for example,

$$C_6H_5-N_2-C_{10}H_6\overset{\beta}{O}H,$$

dissolves in sulphuric acid with a red-violet colour, probably the same which belongs to the mother substance,

$$C_6H_5-N_2-C_{10}H_7.$$

The same colour is obtained if a sulpho-group occurs in the benzene ring; while, on the other hand, if this group is in the naphthol, the compound dissolves with a yellow colour, the same as azobenzene.

These phenomena may be explained on the assumption that the sulpho-group exerts a salt-forming action with one nitrogen atom of the azo-chain; and that in one case with the above compound, the nitrogen atom attached to the benzene ring is influenced, in the other that combined with the naphthalene.

These colour-reactions become more complicated if several azo-groups are present in the molecule.

Substituted azo-compounds are generally prepared by the action of diazo-compounds on phenols and amines. With the latter bodies the intermediate formation of diazo-amido compounds is often observed.

Experience has proved that the azo-group enters in the para-position to the amido- or hydroxyl-group if this is free; if this point is already substituted, the linkage takes place in the ortho-position. Condensations in the meta-position have till now not been observed.

Some azo-compounds may be converted into easily oxidisable hydrazo-compounds by cautious reduction, while all are decomposed by the action of energetic reducing agents. In this case the linkage between the nitrogen atoms is dissolved, each atom being converted into an amido-group by addition of hydrogen. Azobenzene yields on reduction two molecules of aniline; amidoazobenzene gives one molecule of aniline and one molecule of paraphenylenediamine,

$$C_6H_5N=N-C_6H_4NH_2+4H=C_6H_5NH_2+H_2N-C_6H_4-NH_2.$$

This splitting up forms in many cases a means for recognition of azo-compounds and for determining their constitution. By far the greater number of azo-dyestuffs used technically are sulphonic acids, while the number of basic azo-dyes is limited. Amidoazo-compounds of weak basic properties are not easily fixed in dyeing; they yield, however, useful basic dyestuffs if a second amido-group is introduced into the ring, which already contains the auxochrome group. Probably this second group does not act as an auxochrome; it has no connection with the azo-chain, and its function is apparently to supply the necessary attraction for the fibre. If both amido-groups are in different rings, the resulting compound acts as a simple amidoazo-compound.

Chrysoïdine,

$$C_6H_5-N_2-C_6H_3(NH_2)_2,$$

for example, is a strong basic dyestuff, while in an isomer parazoaniline,

$$NH_2C_6H_4-N_2-C_6H_4NH_2,$$

this property is absent. Probably in the latter case both amido-groups are influenced to a certain extent by the azo-chain, while with chrysoïdine this is only the case with one group.

The amido-groups acting as auxochromic groups are therefore probably connected with the azo-group, and when combined with acids to form salts show a striking alteration in colour, while the amido-groups, which play merely a basic part, do not undergo this change.

Chrysoïdine, a case in point, forms stable salts with one molecule of acid, and their colour is little different to that of the base, while with an excess of acid a red di-acid salt is formed, which loses the second molecule of acid on treatment with water. On the other hand, amidoazobenzene forms red salts which are decomposed by water.

Parazoaniline, which in all probability contains two auxochromic amido-groups, shows different colours according as one or both of these groups are saturated. With acids it gives at first a green colour; in presence of excess, however, a red colour.

Certain facts render it doubtful whether the auxochromic amido-groups enter into combination with the acid radical in the formation of salts, and it is possible that the azo-group enters into combination. Amidoazobenzene, a weak base, retains its basic properties after acetylation, and forms red salts as before; while the simple amines such as aniline, which possess much stronger basic properties, yield on acetylation almost completely indifferent compounds. At any rate this fact strongly supports the assumption that there is a certain linkage between the azo- and amido-groups.

The sulphonic acids of the amidoazo-compounds are interesting in this respect. Apparently they are incapable of existing in the free state, at least from their colour it appears that the formation of a salt takes place between the sulpho-group and the basic group.

Amidoazobenzene in the free state is yellow, while its sulphonic acids have the red colour of the amidoazobenzene salts. If, however, the sulpho-group is saturated by an alkali, the salt produced has again the colour of free amidoazobenzene.

These amido-sulphonic acids behave like acid dyestuffs, but in dyeing the fibre always takes the colour of their alkali salts or of the free amidoazo-base.

The conclusions naturally drawn from this are that the sulpho-group effects the combination with the fibre, and that the acid properties of the former are saturated by the latter.

This property is still more striking with the sulphonic acid of phenyl amidoazobenzene (Tropäolin OO); this body exhibits a colour-change from orange to violet.

The azo-compounds, though long known, have attained most of their importance in the last ten years, especially the scarlet-red shades, which have almost entirely replaced cochineal. The first azo-dyestuff used largely was triamidoazobenzene (phenylene brown) discovered by Caro and Griess in 1867.

For ten years after this no particular progress was made in this field, and the first synthetical production of azo-compounds appears with the discovery of chrysoïdine by Witt and Caro.

Chrysoïdine was rapidly followed by the introduction of the acid dyestuffs, discovered almost simultaneously by Witt and Roussin, and which, since the introduction of naphthols, have attained great importance.

The manufacture of azo-dyes is in general very simple. If a diazo-compound has to be combined with a phenol, the former is prepared by dissolving the amine or its sulphonic acid in water, or suspending them in as finely divided a state as possible, and adding to the liquid the calculated quantities of hydrochloric acid and sodium nitrite.

After diazotisation is completed the liquid is allowed to run into an alkaline solution of the phenol or its sulphonic acid, care being taken that the mixture remains alkaline. After some time the dyestuff is salted out, and is generally filtered through a filter-press. The combination of diazo-compounds with amines is somewhat more complicated. Some of these, for instance metaphenylenediamine, combine with diazo-compounds in neutral aqueous solutions; while others, like diphenylamine, are dissolved in alcohol, and a concentrated solution of the diazo-compound gradually added. In the manufacture of amidoazobenzene and all compounds in which an intermediate formation of a diazo-amido-compound takes place, a large excess of the amine has to be employed, to hold the diazoamido-compound formed in solution.

Sulphonic acids are generally obtained by combination of diazo-sulphonic acids with phenols or diazo-bases with phenolsulphonic acids, in a few cases also by heating the azo-compound with fuming sulphuric acid.

The principal application of azo-dyestuffs is in wool-dyeing, and all acid azo-dyes may be directly dyed on animal fibres from an acid bath.

On cotton they are generally incapable of complete fixation, as most of them form no real colour-lakes. Exceptions to this rule are certain tetrazo-compounds which dye cotton directly in the form of alkali salts of their sulphonic acids.

Basic azo-dyes (chrysoïdine, Bismark brown) are dyed like all colour-bases on vegetable fibres prepared with tannic acid. Their principal application is in cotton-dyeing.

A uniform method of nomenclature for all azo-compounds is much to be desired, but the strict application of such a principle, further than formation into groups, would lead to the necessity for very long, and often unwieldy names, without insuring certainty in regard to position.

For this reason such a method has been avoided, and the bodies are in general described under the names given them by their discoverers.

I. AMIDOAZO-COMPOUNDS.

Amidoazobenzene [5, 6].

$$C_6H_5-N=\overset{(1)}{N}-C_6H_4\overset{(4)}{N}H_2.$$

Amidoazobenzene is formed by the molecular transformation which diazoamidobenzene undergoes when brought in contact with aniline hydrochloride, best in aniline solution. It is therefore the final product of the reaction which occurs when a salt of diazobenzene is treated with an excess of aniline, at a medium temperature.

Its manufacture on a large scale depends on this principle: Aniline is treated with such quantities of hydrochloric acid and sodium nitrite, that about a third is converted into diazoamidobenzene, and that the latter remains dissolved in the excess of aniline. Further, the amount of hydrochloric acid is so calculated, that after decomposition of the nitrite some aniline hydrochloride remains in the mixture. The conversion of the diazoamidobenzene is aided by warming gently, and, when complete, the excess of aniline is saturated with dilute hydrochloric acid, and filtered from the sparingly soluble amidoazobenzene hydrochloride.

Free amidoazobenzene forms yellow needles melting at 127°·5, which may partly be sublimed without decomposition.

Its salts with acids are red and very unstable. They crystallise well, and possess a bluish reflex. They are decomposed by water, and are difficultly soluble in dilute acids, a red solution being produced. With concentrated sulphuric acid, amidoazobenzene gives a yellowish-brown solution. It is easily split up on reduction, aniline and paraphenylenediamine being formed.

By cautious treatment with zinc powder in alkaline solution it is converted into amidohydrazobenzene, a colourless compound which oxidises rapidly on exposure to the air.

Amidoazobenzene itself is useless as a dyestuff, but is important as a starting-point for the manufacture of various dyestuffs.

An isomer of amidoazobenzene, which contains the amido- and azo-groups in the ortho position, has recently been obtained by Janovsky [7].

Amidoazobenzenemonosulphonic Acid [8, 9].

$$\mathrm{H\overset{(1)}{S}O_3C_6H_4-\overset{(4)}{N}=\overset{(1)}{N}-C_6H_4N\overset{(4)}{H}_2.}$$

This acid is obtained with the disulphonic acid by treating amidoazobenzene with fuming sulphuric acid. It is formed in small quantities by the action of paradiazobenzenesulphonic acid on aniline hydrochloride. It may also be obtained by cautious reduction of nitroazobenzenesulphonic acid.

As obtained by decomposition of its salts with hydrochloric acid, it forms a gelatinous flesh-coloured precipitate, which after some time changes to needles. Its salts throughout are sparingly soluble in cold water, but dissolve easily in hot water. The sodium salt forms golden-yellow leaflets.

Amidoazobenzenedisulphonic Acid [8, 9].

$$\mathrm{H\overset{(1)}{S}O_3\,.\,C_6H_4\overset{(4)}{N}=\overset{(1)}{N}-C_6H_3N\overset{(4)}{H}_2SO_3H.}$$

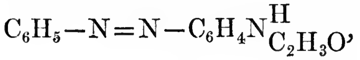
This acid is produced by the energetic action of fuming sulphuric acid on amidoazobenzene. It forms shimmering violet crystals resembling chromic chloride, which on drying disintegrate.

The acid is easily soluble in water, but separates on addition of a mineral acid. Its salts are yellow, very easily soluble, and difficult to crystallise.

The sulpho-groups are present in both rings, and on reduction the body yields sulphanilic and paraphenylenediaminesulphonic acids.

Both these sulphonic acids of amidoazobenzene, and especially the disulphonic acid, are valuable yellow dyestuffs, and the sodium salt of the latter comes into commerce as Acid Yellow or Fast Yellow. A further application of these acids is in the preparation of tetrazo-dyestuffs, for example Biebrich- and Croceïn-scarlets.

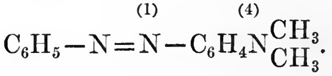
Acetylamidoazobenzene [71],



$$C_6H_5-N=N-C_6H_4N\begin{matrix}H\\C_2H_3O\end{matrix},$$

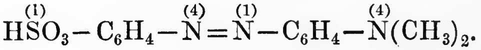
forms yellow leaflets melting at 141°. It dissolves in hydrochloric acid with a red colour, and is only saponified on boiling.

Dimethylamidoazobenzene [10].



$$C_6H_5-\overset{(1)}{N}=N-\overset{(4)}{C_6H_4}N\begin{matrix}CH_3\\CH_3\end{matrix}.$$

Dimethylamidoazobenzenesulphonic Acid [11].



$$H\overset{(1)}{S}O_3-C_6H_4-\overset{(4)}{N}=\overset{(1)}{N}-C_6H_4-\overset{(4)}{N}(CH_3)_2.$$

Dimethylamidoazobenzene is obtained by action of dimethylaniline on hydrochloride of diazobenzene, and if the latter be replaced by diazobenzenesulphonic acid, the above monosulphonic acid is formed.

The base forms golden-yellow leaflets melting at 115°. Its hydrochloride, $C_{14}H_{13}N_3,HCl$, forms violet needles sparingly soluble in water. The basic character of amidoazobenzene seems to be increased by introduction of alcohol radicals into the amido-group, as the salts of dimethylamidoazobenzene are far more stable than those of amidoazobenzene. A dilute solution of the base becomes reddened by a trace of acid, and on this fact depends its application as an indicator in alkalimetry. Acetic acid and amidosulphonic acids are without action on the compound. Dimethylamidoazobenzene is sometimes used for colouring butter and candles.

The monosulphonic acid forms brilliant violet needles, which are sparingly soluble. Its salts are yellow, and mostly well crystallised.

The calcium salt is obtained as a lustrous precipitate by adding calcium chloride to a solution of the sodium salt.

The sodium salt of this sulphonic acid has been used as a dyestuff under the names Tropäolin II, Orange III, and Helianthine. It gives fine orange shades on wool and silk, but owing to its sensitiveness towards acids has not met with great success.

Phenylamidoazobenzene [12],

$$C_6H_5-N=N-C_6H_4NHC_6H_5,$$

is formed by the action of diazobenzene chloride on diphenylamine. It crystallises in golden-yellow prisms or leaflets. M.P. 82°.

It is soluble in alcohol, ether, benzene, and ligroine, insoluble in water. Acids colour the alcoholic solution violet, the salts being precipitated as grey crystals. It dissolves in concentrated sulphuric acid with a green colour, changing through blue to violet on dilution with water. By action of amyl nitrite a nitrosamine, M.P. 119°·5, is obtained. On reduction it yields aniline and paramidodiphenylamine.

Phenylamidoazobenzenesulphonic Acid [12].

$$H\overset{(1)}{S}O_3-C_6H_4\overset{(4)}{N}=N-C_6H_4NHC_6H_5.$$

(Tropäolin OO, Orange IV.)

Is obtained by action of p-diazobenzenesulphonic acid on an acid, alcoholic, diphenylamine solution. The free acid forms needles resembling graphite, which dissolve sparingly in water with a red-violet colour. The salts are well crystallised, and, with the exception of the insoluble calcium and barium salts, dissolve easily in hot water, less easily in cold water. Concentrated sulphuric acid dissolves the compound, forming a violet solution. The sodium salt has a large application, and comes into commerce under the above designations. It dyes wool and silk a beautiful orange.

An isomeric compound prepared from metamidobenzenesulphonic acid is known as Metanil Yellow and dyes somewhat yellower shades.

Yellow dyestuffs are also obtained by action of diazotoluenesulphonic acids on diphenylamine.

Nearly all phenylamidoazo-compounds yield nitro-derivatives when their nitrosamines are carefully treated with nitric acid. The nitro-group enters into the diphenylamine, and certain bodies obtained in this manner are used under the names Azoflavine, Citronine, and Indian Yellow. They are distinguished from the original dyestuffs by their yellower shade.

Experimental trials have also been made with higher sulphonic acids of phenylamidoazobenzene.

Amidoazotoluenebenzene [13].

$$C_6H_4\overset{(1)}{C}H_3-\overset{(4)}{N}=\overset{(1)}{N}C_6H_4\overset{(4)}{N}H_2.$$

From paradiazotoluene and aniline. Forms long yellowish-brown needles melting at 147°.

Amidoazotoluenes.

A. $C_6H_4\overset{(1)}{C}H_3-\overset{(2)}{N}=\overset{(1)}{N}-C_6H_3\overset{(3)}{C}H_3\overset{(4)}{N}H_2.$ [13]

Is obtained from orthotoluidine in a similar manner to amidoazobenzene from aniline. M.P. 100°.

B. $C_6H_4\overset{(1)}{C}H_3-\overset{(4)}{N}=\overset{(1)}{N}-C_6H_3\overset{(3)}{C}H_3\overset{(4)}{N}H_2.$ [13]

From paradiazotoluene and orthotoluidine. M.P. 127–128°.

C. $C_6H_4\overset{(1)}{C}H_3-\overset{(3)}{N}=\overset{(1)}{N}-C_6H_3\overset{(2)}{C}H_3\overset{(4)}{N}H_2.$ [13]

From metatoluidine. M.P. 80°.

D. $C_6H_4\overset{(1)}{C}H_3-\overset{(4)}{N}=\overset{(1)}{N}-C_6H_3\overset{(2)}{C}H_3\overset{(4)}{N}H_2.$ [13]

By the action of paradiazoamidotoluene on metatoluidine. M.P. 127°.

E. $C_6H_4\overset{(1)}{C}H_3-\overset{(4)}{N}=\overset{(1)}{N}-C_6H_3\overset{(4)}{C}H_3\overset{(2)}{N}H_2.$ [14]

By the interaction of paradiazoamidotoluene and paratoluidine. M.P. 118°·5.

These amidoazotoluenes, when treated with fuming sulphuric acid, yield sulphonic acids, some of which are used as yellow dyestuffs.

The first four amidoazotoluenes, A, B, C, D, contain the amido-group in the para position to the azo-group. They are all reddened by acids, and yield paradiamidotoluene on reduction.

The last compound, E, contains the groups in the ortho position; it is coloured green by acids, and yields orthodiamidotoluene on reduction.

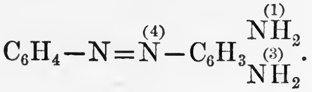
Amidoazoxylenes.

Seven isomeric amidoazoxylenes are known, but for a description reference must be made to the literature of the subject [15, 16].

Generally speaking, their properties are similar to those of amidoazobenzene and the amidoazotoluenes.

Diamidoazobenzenes [12, 13].

A. *Chrysoïdine* [17, 18].



$$C_6H_4-N=\overset{(4)}{N}-C_6H_3\begin{array}{l}\overset{(1)}{NH_2}\\ {\scriptstyle(3)}\\ NH_2\end{array}.$$

Chrysoïdine is prepared by mixing equivalent quantities of solutions of diazobenzene chloride and metaphenylenediamine. The base crystallises from hot water in yellow needles, M.P. $117^{\circ}\cdot5$. It dissolves sparingly in water, easily in alcohol, ether, and benzene [18].

It forms two series of salts with acids [18]; the monoacid salts are stable and yellow in solution, the diacid salts are red and are decomposed by water.

$C_{12}H_{13}N_4,HCl$ is obtained in two forms according to whether it has been crystallised rapidly or slowly. In the first case it forms long red felted needles, and in the latter anthracite black aggregates of octahedrons possessing a green reflex. With an excess of hydrochloric acid, $C_{12}H_{13}N_4(HCl)_2$ is obtained, a salt soluble with a red colour, but decomposed by water.

On reduction chrysoïdine splits up, aniline and triamidobenzene being produced.

$C_{12}H_{11}N_4(C_2H_3O)_2$ is formed by warming chrysoïdine with acetic anhydride; forms yellow prisms, M.P. 250° [18].

It yields a dimethyl derivative on warming with methyl iodide.

Tetramethylchrysoïdine has been prepared by the action of diazobenzene chloride on tetramethylphenylenediamine.

A sulphonic acid may be obtained by treating chrysoïdine with fuming sulphuric acid, or by allowing paradiazobenzenesulphonic acid to react with metaphenylenediamine.

Chrysoïdine, which was discovered by Witt, is one of the few basic azo-dyestuffs, and like all basic colouring-matters dyes cotton mordanted with tannic acid. Its principal application is in cotton-dyeing, especially for shading purposes. It gives a yellowish-orange colour.

It is of historical interest, as being the first azo-dyestuff prepared by a direct synthesis.

B. *Symmetrical* Di *Amidoazobenzene* [19, 20].

Parazoaniline,

$$\overset{(1)}{N}H_2-C_6H_4-\overset{(4)}{N}=\overset{(1)}{N}-C_6H_4-\overset{(4)}{N}H_2,$$

is formed by saponification of the acetyl compound described below, and by reduction of the compound obtained by action of paranitrodiazobenzene on aniline.

It forms long, flat, yellow needles. M.P. 140°.

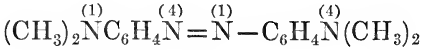
It is sparingly soluble in water and benzene, easily in alcohol.

The monoacid salts dissolve in alcohol with a green colour, while the diacid salts give a red solution.

Acetyl derivative [20], $C_{12}H_{11}N_4(C_2H_3O)$, is obtained by the interaction of aniline and paradiazoacetanilide in presence of a little hydrochloric acid. M.P. 212°. Its salts dissolve with a red colour.

Diacetyl derivative, $C_{12}H_{10}N_4(C_2H_3O)_2$, is formed on reduction of paranitroacetanilide with zinc powder and alcoholic ammonia [19]. It forms yellow needles. M.P. 282°.

Tetramethyl derivative [21],

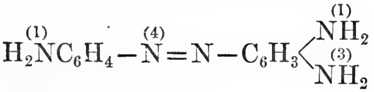


$$(CH_3)_2\overset{(1)}{N}C_6H_4\overset{(4)}{N}=\overset{(1)}{N}-C_6H_4\overset{(4)}{N}(CH_3)_2$$

(Azyline), is formed by the action of nitric oxide on dimethylaniline, and by action of paradiazodimethylaniline on the same amine [22].

Diphenine of Gerhardt and Laurent [23] and hydrazoaniline of Haarhaus [24] are regarded as hydrazo-compounds; they are probably diamidoazo-compounds, as they possess tinctorial properties in a marked degree, which is not usual in hydrazo-compounds.

Triamidoazobenzene.

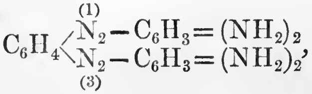


$$H_2\overset{(1)}{N}C_6H_4-\overset{(4)}{N}=N-C_6H_3\left\langle\begin{matrix}\overset{(1)}{N}H_2\\ \scriptstyle(3)\\ NH_2\end{matrix}\right.$$ [25].

(Phenylene Brown, Vesuvine, Bismark Brown.)

Triamidoazobenzene forms brownish-yellow warty crystals, which dissolve sparingly in cold water, easily in hot water. M.P. 137°. Acids colour the brownish-yellow solution reddish brown, and produce diacid salts.

Triamidoazobenzene is formed along with other azo-compounds, on treating metaphenylenediamine with nitrous acid. Its hydrochloride forms the principal constituent of the dyestuffs known under the above names. (A more recent view is that Bismark brown consists partly at least of a compound of the formula



$$C_6H_4\left\langle\begin{matrix}\overset{(1)}{N_2}-C_6H_3=(NH_2)_2\\ \underset{(3)}{N_2}-C_6H_3=(NH_2)_2,\end{matrix}\right.$$

which is to be regarded as a metaphenylenediamine disazometaphenylenediamine.)

With the exception of chrysoïdine, Bismark brown is the only basic azo-dyestuff in practical use. It is used in dyeing cotton and leather.

Diamidoazotoluenes. [See 26, 27.]

Benzeneamidoazonaphthalene [28, 29],

$C_6H_5N{=}N{-}C_{10}H_6NH_2\,\alpha$,

is obtained by interaction of diazobenzene chloride and α-naphthylamine.

Sulphonic acids may be obtained by action of paradiazobenzenesulphonic acid on α and β naphthylamine.

A corresponding toluene compound has been prepared by action of paradiazotoluene on α-naphthylamine [27].

The dyestuff known as orchil substitute or orseilline is prepared by action of paranitrodiazobenzene on naphthionic acid (α-naphthylaminesulphonic acid). It produces reddish-brown shades on wool and is dyed from an acid bath [72].

Amidoazonaphthalene,

$\alpha\,C_{10}H_7N{=}N{-}C_{10}H_6NH_2\,\alpha$ [30],

is formed by action of nitrous acid on excess of α-naphthylamine, and is best prepared by mixing a solution of two molecules of α-naphthylamine hydrochloride with one molecule of sodium nitrite. The base forms reddish-brown needles, which show a green reflex; it melts at 175°, and is sparingly soluble in alcohol, readily in xylene.

The salts dissolve in alcohol with a violet colour, and are decomposed by water.

The azo-group is present in the α para position to the amido-group.

Sulphonic acids of this compound are obtained by direct sulphonation, or by combination of diazonaphthalenesulphonic acid with α-naphthylamine.

A disulphonic acid of amidoazonaphthalene is obtained by action of sodium nitrite on naphthionic acid; its constitution differs from that of the above acids, as the second α-position usually taken by the azo-group is occupied by the sulpho-group in naphthionic acid.

The corresponding β-amidoazonaphthalene is obtained in a similar manner from β-naphthylamine; it melts at 156°, and is a slightly weaker base.

Mixed amidoazonaphthalenes have also been prepared.

II. OXYAZO-COMPOUNDS.

Oxyazobenzene [31, 32, 33].

$$C_6H_5-N=\overset{(1)}{N}-C_6H_4\overset{(4)}{O}H.$$

(*Phenoldiazobenzene.*)

Oxyazobenzene is prepared by interaction of diazobenzene chloride and phenol-sodium [32], and is also formed by action of barium carbonate on salts of diazobenzene [31].

It may further be obtained by treating the isomeric azoxybenzene with sulphuric acid [34], and by the action of nitrosophenol on aniline [33].

It forms needles, M.P. 151°; it is slightly soluble in water, easily in alkalies and in alcohol.

Parasulphonic acid—

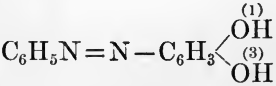
$$H\overset{(1)}{S}O_3-C_6H_4-\overset{(4)}{N}=\overset{(1)}{N}-C_6H_4OH,$$

may be obtained by direct sulphonation, or by action of paradiazobenzenesulphonic acid on phenol-sodium.

This compound was formerly in commerce as Tropäolin Y, but owing to its dull brownish shade was soon displaced. An isomeric metasulphonic acid is formed by action of metadiazobenzenesulphonic acid on phenol-sodium [36].

Dioxyazobenzene [35].

a. Unsymmetrical:—

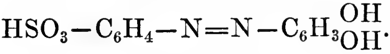


$$C_6H_5N=N-C_6H_3\begin{cases}\overset{(1)}{OH}\\ \overset{(3)}{OH}\end{cases}$$

This compound is prepared by action of diazobenzene chloride on resorcin in presence of an alkali.

It forms red needles, M.P. 161°; and is soluble in alcohol, ether, and alkalies.

Parasulphonic Acid.



$$HSO_3-C_6H_4-N=N-C_6H_3\begin{smallmatrix}OH\\OH\end{smallmatrix}.$$

(TROPÄOLIN O.)

This dyestuff is prepared by action of paradiazobenzenesulphonic acid on resorcin [36, 37], and is also formed by sulphonation of dioxyazobenzene [37].

The free acid forms needles, which appear almost black with a greenish lustre by reflected light, and red by transmitted light. It is a strong acid, capable of liberating hydrochloric acid from a solution of common salt, thereby forming a sodium salt.

The salts are orange-yellow, and are only decomposed by concentrated hydrochloric acid or by dilute sulphuric acid.

Tropäolin O is a strong dyestuff, producing a fine golden-yellow shade on wool and silk, being dyed from an acid bath. It was formerly used in silk-dyeing.

The metasulphonic acid is obtained from metadiazobenzenesulphonic acid and resorcin [36].

β. *Symmetrical dioxyazobenzenes* (AZOPHENOLS) [38] :—

a. *Para-azophenol*

is formed on melting paranitro- or nitrosophenol with potash, M.P. 204°.

b. *Ortho-azophenol*

is formed similarly from orthonitrophenol, M.P. 171°.

Oxyazobenzenetoluene [33],

$$CH_3C_6H_4-N=N-C_6H_4OH,$$

(*Phenolazotoluene.*)

is obtained from nitrosophenol and paratoluidine, M.P. 151°.

Cumeneazoresorcin,

$$(CH_3)_3C_6H_2-N=N-C_6H_3(OH)_2,$$

from diazocumene and resorcin [39], M.P. 199°.

Amido-oxyazobenzene [40],

$$\overset{(1)}{H_2N}C_6H_4-\overset{(3)}{N}=\overset{(1)}{N}-C_6H_4(\overset{(4)}{OH}) \text{ (M.P. } 168^\circ\text{)},$$

is obtained by saponification of the acetyl-compound

$$C_2H_3ONH-C_6H_4-N=N-C_6H_4OH \text{ (M.P. } 208^\circ\text{)},$$

which is prepared by interaction of phenol-sodium and the diazo-compound from monoacetylmetaphenylenediamine.

Oxyazo-compounds are also obtained by action of diazo-compounds on the isomeric cresols [39, 41, 42].

α-Azonaphthalene-resorcin [46],

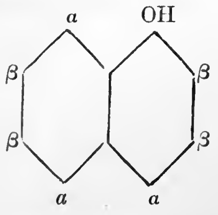
$$C_{10}H_7-N=N-C_6H_3(OH)_2,$$

forms red needles, M.P. about 200°.

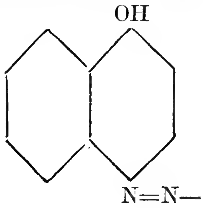
NAPHTHOLAZO-DYESTUFFS.

These dyes belong to the oxyazo series, and have within the last ten years attained enormous importance, on account of the beauty of their shades and their strong tinctorial properties. For these, and other reasons, they are worthy of being studied as a separate class.

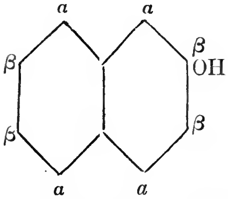
The isomeric naphthols combine with all diazo-compounds, producing azo-compounds, and with α-naphthol



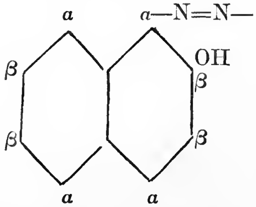
the azo-chain enters into the second α-position of the substituted ring. This is exactly analogous to the formation of the corresponding compounds with benzene derivatives containing a free para position. The simplest α-naphthol azo-compounds are constituted as expressed by the following formula:



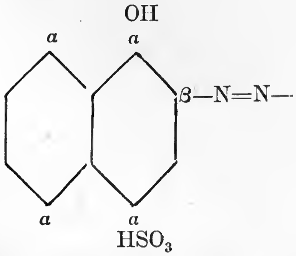
β-naphthol



has no free para position and the azo-group enters in the ortho position, viz. in the adjacent *a*-position:

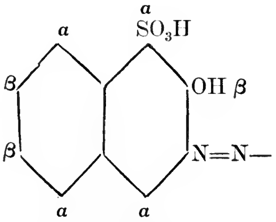


The case is different when these positions are already occupied by other groups, for example, by the sulpho-group. With *a*-naphthol the azo-chain enters into the adjacent β-position; for instance, with *a*-naphtholsulphonic acid azo-compounds of the general formula



are formed.

The formula with β-naphthol:



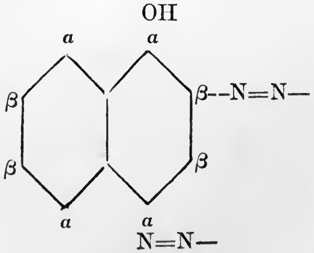
is probably correct, but has not been proved to be absolutely certain. In general, azo-compounds containing the chromophoric and auxochromic groups in the ortho position are far more valuable as dyes than their allies of the para-series.

The latter have the undesirable property of altering their shade on treatment with alkalies or acids in a much higher degree than the former compounds. This applies equally to oxy- and amido-azo-compounds, especially those of the naphthol series.

For this reason β-naphthol gives more useful dyestuffs than α-naphthol.

The derivatives of the latter exhibit striking changes in colour on treating with alkalies.

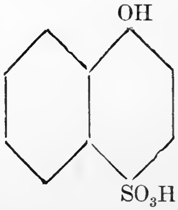
If, however, the para position in α-naphthol is substituted, as in the α α-sulphonic acid, the azo-group enters in the β- (ortho) position, and stable and useful dyes are obtained. Diazo-compounds are capable of reacting on β-naphthol once, while α-naphthol, like phenol, reacts with two molecules of a diazo-compound. In the resulting dis-azo bodies the second azo-group is probably in the β 1-position, as expressed in the following formula:



The naphthol azo-dyes are almost exclusively applied in form of their sulphonic acids. These may be obtained by combination of sulphonated diazo-compounds with naphthols, or of diazo-compounds with naphtholsulphonic acids.

The sulpho-group of the diazo-compound has little or no influence in the shade of the dyestuff, but the isomeric naphtholsulphonic acids are capable of giving totally different dyestuffs with the same diazo-compound. In most cases this may be attributed to the different positions of the azo-group already mentioned. It is necessary for a correct comprehension of the following dyestuffs to consider the principal naphtholsulphonic acids somewhat more closely, for although our knowledge in this direction is incomplete, many valuable researches have been made in recent years, of which those of Armstrong are especially worthy of mention.

At present three monosulphonic acids have been obtained from α-naphthol, but the constitution of only one of these is known with any degree of certainty. This is the $\alpha\,\alpha$-acid prepared by Nevile and Winther, and studied more closely by Witt. It is obtained by decomposition of the diazo-compound of naphthionic acid with water, and from its method of formation is constituted according to the formula:



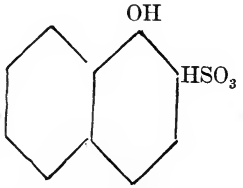
This formula agrees well with the nature of the dyestuffs obtained from this acid; they are totally different to the simple α-naphthol dyes, as the azo-group enters in the β 1 position and not in the α 2.

The dyestuffs from α-naphthol and diazo-compounds of the benzene series are orange or brown, while those from the $\alpha\,\alpha$-acid are mostly of a beautiful *ponceau*-red tone.

A second acid was prepared by Schaeffer, in 1869, who probably obtained it mixed with the $\alpha\,\alpha$-acid.

Schaeffer's acid is obtained along with the latter acid by heating α-naphthol with concentrated sulphuric acid on the water-bath. It differs from the $\alpha\,\alpha$-acid by the sparing solubility of its sodium-salt in alcohol, and more especially by the dyestuffs it yields. These are analogous to the corresponding α-naphthol derivatives, and therefore very probably para-compounds.

The acid has probably the constitution expressed by the following formula:



as it yields dinitronaphthol on treating with nitric acid, and phthalic acid on oxidation.

A third acid has been prepared by Baum, but little is known of its constitution. [Patent, 1883, No. 3498. Provisional Specification.]

Claus and Oehler have examined an acid [75] to which they ascribe the constitution $a_1\ a_2$, but it is doubtful whether it is identical with the Schaeffer or with the Nevile-Winther acid.

It may be as well to take this opportunity of remarking that a method often used for determining the constitution of naphtholsulphonic acids appears not to be trustworthy, as molecular changes, which occur so frequently in the naphthalene series, appear to take place here also. This is the method depending on the conversion of the acids into chloronaphthalenes by means of phosphorus pentachloride. Indeed the results so obtained often differ from all others.

The Schoellkopf Aniline Co. have patented an acid obtained by nitration of a-naphthalenemonosulphonic acid, reduction to amido-acid, and conversion into naphtholsulphonic acid by the diazo-reaction. It is so far characteristic as it gives a scarlet with diazotoluene, while its isomers give oranges. [D.P. 15871.]

a-naphthol also yields a disulphonic acid (?), and a trisulphonic, which, however, have no importance in the manufacture of azodyes.

β-naphthol, on treating with sulphuric acid, gives in the first instance three monosulphonic acids.

One of these (the a-sulphonic acid or croceïn-acid) is best obtained at a low temperature. By further heating with sulphuric acid it goes over into the β- or Schaeffer's acid, which was prepared by Schaeffer a long time ago. These acids are distinguished principally by the different solubilities of their disodium compounds:

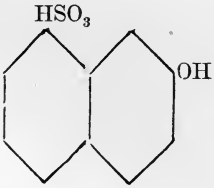
$$C_{10}H_6\left\langle\begin{matrix}SO_3Na\\ONa\end{matrix}\right. .$$

The basic salt of the α-acid is easily soluble in hot alcohol, while that of the Schaeffer acid is almost insoluble.

The third acid, which has only recently been identified by its conversion into the corresponding β-naphthylaminesulphonic acid, is identical with the F- or δ-acid. [Green: B. B. 1889, p. 721.]

From the facts that azo-dyes from Schaeffer's acid differ but little in shade and solubility from those obtained from β-naphthol, and that simple β-naphthol azo-compounds on sulphonation always yield derivatives of Schaeffer's acid, and never those of croceïn-acid, it may naturally be concluded that the azo-group enters in the same position both in β-naphthol and in Schaeffer's acid. This is the α_1 position.

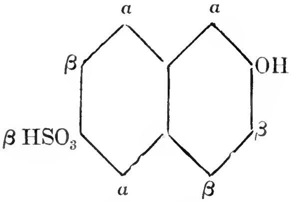
The behaviour of the α-acid is totally different. The dyestuffs do not resemble those from Schaeffer's acid and β-naphthol in the least, either as regards shade or solubility. Further, this acid may easily be converted into a dinitro-compound with nitric acid, and this is not the case with either β-naphthol or Schaeffer's acid. Another striking property of the α-acid is that its combination with diazo-compounds takes place with much more difficulty than is experienced with Schaeffer's acid. Its constitution is therefore



justifying the designation β-naphthol-α-monosulphonic acid for this acid. The conversion of the corresponding β-naphthylamine-sulphonic acid into α-naphthalenesulphonic acid also shows that it is really an α-acid.

Schaeffer's acid yields sulphophthalic acid on oxidation, showing that the hydroxyl and sulpho-groups are in different rings.

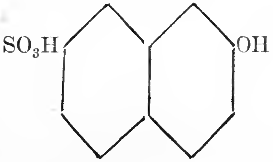
Noelting ascribes the following constitution to Schaeffer's acid :



A third sulphonic acid is that of Cassella and Co., prepared by heating naphthalene-*a*-disulphonic acid with caustic alkali.

This acid is technically known as F-acid, and is identical with the acid prepared by the diazo-reaction from Bayer's β-naphthylamine-δ-sulphonic acid.

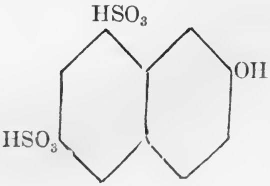
Without doubt it has the constitution :



It is without importance for preparing azo-dyes.

Of the β-naphtholdisulphonic acids, three are used in the colour-industry [73, 74]. Two of these are formed by energetic action of sulphuric acid on β-naphthol, and may be separated by taking advantage of the different solubilities of their sodium salts in alcohol or in concentrated salt-solution.

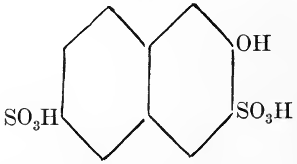
The acid soluble in alcohol and salt-solution (G-acid of Meister, Lucius, and Brüning, γ-acid of Cassella and Co.) behaves very like β-naphthol-*a*-monosulphonic acid (croceïn acid), and must be regarded as a derivative of the latter, as it is formed quantitatively on further sulphonation of croceïn acid. It may also be obtained from Schaeffer's acid (this is contradicted by some chemists), and Armstrong gives it the following formula :—



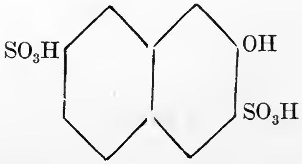
The azo-dyes from G-acid are yellowish and easily soluble, and are very similar to those from the *a*-monosulphonic acid.

The disulphonic acid from the sodium salt, sparingly soluble in alcohol and salt-solution (R-acid, Meister, Lucius, and Brüning), gives dyestuffs of considerably bluer shade, and also more difficultly soluble. They are, however, very important.

This R-acid is best obtained by further sulphonation of Schaeffer's acid, and it is also stated that G-acid is converted into R-acid on heating with sulphonic acid. The constitution of the R-acid is expressed by the formula :—



Another disulphonic acid, β-naphthol-δ-disulphonic acid is prepared by further sulphonation of the F-acid. It has the constitution



A β-naphtholtrisulphonic acid is obtained by sulphonation of β-naphthol with fuming sulphuric acid at a high temperature. It has been used for the preparation of azo-colours.

Azobenzene-α-naphthol [1],

$$C_6H_5-N=N-C_{10}H_6OH\ \alpha,$$

is prepared by action of diazobenzene chloride on an alkaline solution of β-naphthol. It forms yellow leaflets, which dissolve in alkalies with a violet colour.

Monosulphonic Acid [11].

$$\overset{(1)}{HSO_3}-C_6H_4-\overset{(4)}{N}=N-C_{10}H_6OH\ \alpha.$$

(ORANGE I. TROPÄOLIN OOO No. 1.)

This dyestuff is prepared by action of paradiazobenzenesulphonic acid on α-naphthol. The free acid forms almost black leaflets, with a green reflex, which dissolve in concentrated sulphuric acid with a violet coloration. Its alkali salts are orange-yellow, and dissolve easily in water. The solutions become red with excess of alkali (distinction from β-naphthol dyestuffs).

The sodium salt is used in dyeing under the above names.

It dyes wool and silk in an acid bath, producing an orange shade, which is somewhat redder and not so bright as that obtained with the corresponding β-naphthol orange. The calcium salt is amorphous and insoluble. Owing to the sensitiveness which these dyestuffs exhibit towards alkalies, the β-naphthol derivatives are of considerably more importance.

Azobenzene-β-naphthol [1].

$$C_6H_5N=N-C_{10}H_6\overset{\beta}{O}H.$$

Yellow leaflets, insoluble in alkalies.

Monosulphonic Acids.

i. $\overset{(1)}{HSO_3}-C_6H_4-\overset{(4)}{N}=N-C_{10}H_6OH\ \beta.$

(ORANGE II. TROPÄOLIN OOO No. 2.)

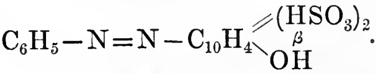
From paradiazobenzenesulphonic acid and β-naphthol. The acid forms orange-yellow leaflets, soluble in water. The crystals on drying lose water and fall to a powder resembling red lead. The alkali salts are similar to the acid, and are unchanged by excess of alkali (distinction from α-naphthol dyestuffs). Its calcium salt dissolves sparingly, the barium salt not at all. The compound dissolves in concentrated sulphuric acid with a magenta-red colour. On wool and silk it gives a beautiful orange, and is one of the most important azo-dyes.

$$\text{ii.}\quad C_6H_5-N=N-C_{10}H_5\overset{\beta}{O}HHSO_3.$$

(CROCEÏN ORANGE.)

From diazobenzene and Schaeffer's β-naphtholmonosulphonic acid (β-acid). The shade of the dyestuff is somewhat yellower than that of the former. It gives an orange-yellow solution with concentrated sulphuric acid.

Disulphonic Acids.



$$C_6H_5-N=N-C_{10}H_4\begin{matrix}\diagup (HSO_3)_2 \\ \diagdown \overset{\beta}{OH}\end{matrix}.$$

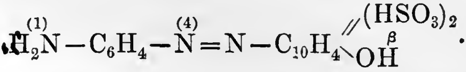
ORANGE G.

Is obtained by the action of diazobenzene on β-naphtholdisulphonic acid (the modification G, soluble in alcohol). It is a yellowish-orange dyestuff, which gives an orange-yellow solution with concentrated sulphuric acid.

SCARLET 2 G.

This dyestuff is an isomer of the above, prepared by action of diazobenzene chloride on the R modification of β-naptholdisulphonic acid.

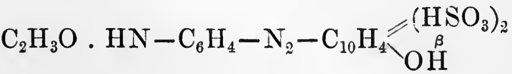
Amidoazobenzene-β-naphtholdisulphonic Acid.



$$\overset{(1)}{H_2N}-C_6H_4-\overset{(4)}{N}=N-C_{10}H_4\begin{matrix}\diagup (HSO_3)_2 \\ \diagdown \overset{\beta}{OH}\end{matrix}.$$

May be obtained by saponification of its acetyl derivative, and by combination of β-naphtholdisulphonic acid (R) with paradiazoaniline [44] (from paraphenylenediamine and one mol. HNO_2). It forms brownish-yellow leaflets, which dissolve in alkalies with a violet colour, becoming red with excess of alkali.

Acetyl derivative :—



$$C_2H_3O\ .\ HN-C_6H_4-N_2-C_{10}H_4\begin{matrix}\diagup (HSO_3)_2 \\ \diagdown \overset{\beta}{OH}\end{matrix}\quad [43].$$

From p-diazoacetanilid and naphtholdisulphonic acid; forms red leaflets.

Dyestuffs obtained by combination of the diazotoluenes and their sulphonic acids with β-naphthol and its sulphonic acids are also of technical value.

AZO-DYES FROM β-NAPHTHOLDISULPHONIC ACIDS AND THE HIGHER HOMOLOGUES OF DIAZOBENZENE [45].

It has already been remarked on p. 53 that the isomeric disulphonic acids of β-naphthol give dyes of totally different shades with diazo-compounds. This is probably caused by the azo-group entering in a different position in the naphthalene nucleus. This property is made use of in the colour-industry. The acid corresponding to the sodium salt soluble in alcohol (G-acid, Meister, Lucius, and Brüning) gives orange-yellow dyes with diazo-compounds of the benzene series, and scarlets with those of the naphthalene series; while the R-acid (Meister, Lucius, and Brüning), from the sodium salt insoluble in alcohol, gives red dye-stuffs with the diazo-compounds of the benzene series, varying in depth according to the molecular weight of the latter [45].

The R-acid, when combined with the diazo-compounds of the xylenes and higher homologues of benzene, gives rise to a series of scarlet dyes, which have a wide application in wool-dyeing under the names Ponceau R, RR, RRR, and G. *a*-diazonaphthalene gives a deep claret-red (Bordeaux B). With diazonaphthalene-sulphonic acid and R-acid, a colouring-matter known as "Amaranth" is obtained. Orthodiazoanisol and its homologues give fine red dyestuffs known commercially as Coccinines.

The dyes from diazo-compounds of the benzene series (Ponceaux R, RR, RRR, and Coccinines) form scarlet powders, which dissolve in strong sulphuric acid with a red colour. They give crystalline calcium salts which are soluble in hot water. Dyestuffs containing naphthalene rests on both sides dissolve in sulphuric acid with blue or violet colour.

The following Table contains the most important dyestuffs prepared from the naphtholdisulphonic acids, excluding those belonging to the tetrazo class, which are mentioned later :—

Ponceau 2 G (Meister, Lucius, & Brüning)	R-acid and diazobenzene.
„ R (Badische Aniline- und Sodafab.).	R-acid and diazopara- and metaxylene (from coml. xylidine).
„ 2 R (Actienges f. Aniline) ..	R-acid and diazometaxylene (pure).
„ 3 R (Meister, Lucius, & Brüning)	R-acid and diazoethylmetaxylene).
„ 3 R (Bad. Aniline- und Sodafab.).	R-acid and diazopseudocumene.
„ 4 R (Actienges f. Aniline) ..	Do.
„ 2 R (Meister, Lucius, & Brüning)	Do.
Bordeaux B (do.)..................	R-acid and diazonaphthalene.
Amaranth (Cassella & Co.)	R-acid and α-diazonaphthalene-sulph. acid.
Bordeaux S (Meister, Lucius, & Brüning)	Do.
Coccinin (Meister, Lucius, & Brüning)	R-acid and diazoanisol.
Phenetol Red (do.)	Do. and diazophenetol.
Anisol Red (do.)	Do. and homologues.
Orange G (Meister, Lucius, & Brüning)	G-acid and diazobenzene.
Ponceau 2 G (Bad. Anil. & Sodaf.) ..	Do. and diazopseudocumene.
Crystal Ponceau (Cassella & Co.)....	Do. and α-diazonaphthalene.

α-Azonaphthalene-β-naphthol.

$$C_{10}H_7-N-N_2-C_{10}H_6\overset{\beta}{O}H$$ (α-β-oxyazonaphthalene).

Is obtained by interaction of α-diazonaphthalene chloride and β-naphthol.

Monosulphonic Acid [47].

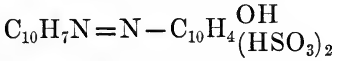
$$HSO_3C_{10}H_6-\overset{\alpha}{N}=N-C_{10}H_6\overset{\beta}{O}H.$$

(FAST RED, ROCCELLINE.)

This is obtained by the action of α-diazonaphthalenesulphonic acid on β-naphthol.

The acid and its sodium salt both form brown needles, sparingly soluble in cold water, easily in hot, separating from the hot solution as gelatinous precipitates. The calcium and barium salts are insoluble and amorphous. The compound possesses very strong tinctorial properties, dyeing wool and silk red. The shade is bluish and not particularly bright. It dissolves in concentrated sulphuric acid with violet colour, separating in brown flocks on dilution.

Disulphonic Acids.

i.  [45].

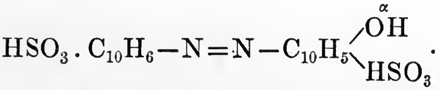
$$C_{10}H_7N{=}N{-}C_{10}H_4\begin{array}{l}OH\\(HSO_3)_2\end{array}$$

a. BORDEAUX B (Meister, Lucius, and Brüning).

From β-naphtholdisulphonic acid (insoluble in alcohol) and α-diazonaphthalene. Gives a blue coloration with strong sulphuric acid.

b. CRYSTAL SCARLET (Cassella & Co.).

Obtained in a similar manner from α-diazonaphthalene and the G- or γ-disulphonic acid (soluble in alcohol). The sodium salt crystallizes very easily.

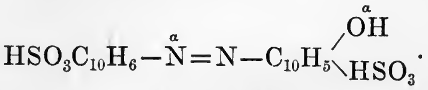
ii. 

$$HSO_3 . C_{10}H_6{-}N{=}N{-}C_{10}H_5\begin{array}{l}\diagup\overset{\alpha}{OH}\\\diagdown HSO_3\end{array}.$$

CROCEÏN SCARLET 3 BX.

From β-naphthol-α-monosulphonic acid [48] and α-diazonaphthalenesulphonic acid. Is a beautiful scarlet dyestuff which dissolves in sulphuric acid with a reddish-violet colour.

Sulphoazonaphthalene-α-naphtholsulphonic Acid.



$$HSO_3C_{10}H_6{-}\overset{\alpha}{N}{=}N{-}C_{10}H_5\begin{array}{l}\diagup\overset{\alpha}{OH}\\\diagdown HSO_3\end{array}.$$

(AZORUBIN.)

This is prepared by combination of α-diazonaphthalenesulphonic acid with the α-naphthol-α-sulphonic acid obtained from the former acid by decomposition with water. It is a fine bluish-red dyestuff. β-naphthylamine and its sulphonic acids are also used in the manufacture of dyestuffs. Oxyazonaphthalene, obtained from β-diazonaphthalene and β-naphthol, is known as "Carminnaphthe," and is used in colouring varnishes.

β-naphthylaminesulphonic acid (Brönner's acid), prepared by heating Schaeffer's β-naphtholmonosulphonic acid with ammonia, gives when diazotised and combined with β-naphthol, a dyestuff used in silk-dyeing. With *a*-naphthol-*a*-sulphonic acid the dye known as Brilliant Scarlet is obtained.

A dyestuff known as Silk-red, or Scarlet for Silk, is prepared by sulphonating β-naphthylamine and diazotising the resulting sulphonic acid and combining with β-naphthol.

III. AZO-DYES FROM DIAZOCARBONIC ACIDS.

Diazo-compounds combine with phenols and amines to form azo-compounds. The tinctorial properties of these bodies are generally weak, becoming intensified, however, by converting the carbonic acids into their ethers.

Dimethylamidobenzene-azo-benzoic Acid [50].

$$COOHC_6H_4-N=N-C_6H_4N(CH_3)_2.$$

Is obtained from m-diazobenzoic acid and dimethylaniline.

Phenolazo-meta-benzoic Acid [49].

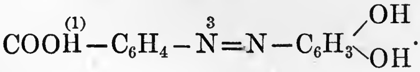
$$COOHC_6H_4-N=N-C_6H_4OH.$$

From diazobenzoic acid and phenol. M.P. 220°.

o-Sulphonic Acid.

From o-phenolsulphonic acid and m-diazobenzoic acid.

Resorcin-azo-benzoic Acid [49].



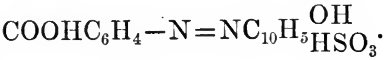
$$COO\overset{(1)}{H}-C_6H_4-\overset{3}{N}=N-C_6H_3\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}.$$

β-Naphthol-azo-benzoic Acid [49].

$$COO\overset{(1)}{H}C_6H_4-\overset{(3)}{N}=N-C_{10}H_6\overset{\beta}{O}H.$$

M.P. 235°. Ethyl ether, M.P. 104° (from diazobenzoic acid ether and β-naphthol).

Monosulphonic Acid [49].



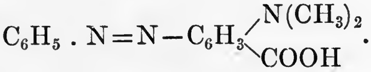
$$COOHC_6H_4-N=NC_{10}H_5\begin{matrix}OH\\HSO_3\end{matrix}.$$

From m-diazobenzoic acid and β-naphtholmonosulphonic acid. Disulphonic and trisulphonic acids have also been prepared by action of m-diazobenzoic acid and its sulpho-acids on β-naphtholdisulphonic acid. Diazoanisic acid, as well as the paradiazocinnamic acid and its ethers [51], gives red azo-dyes [49] with naphthol acid and its sulphonic acids.

IV. AZO-DERIVATIVES FROM CARBONIC ACIDS AND DIAZO-COMPOUNDS.

Oxy- and amidocarbonic acids combine with diazo-compounds to form azo-dyes, some of which possess the property of dyeing on metallic mordants.

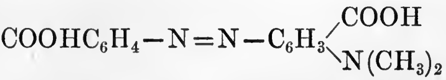
Azobenzene-dimethylamidobenzoic Acid [50, 39].



$$C_6H_5\ .\ N=N-C_6H_3\begin{matrix}/N(CH_3)_2\\ \backslash COOH\end{matrix}.$$

From diazobenzene and dimethyl-m-amidobenzoic acid. M.P. 125°.

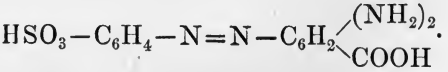
Dimethylamidobenzoic Acid-azobenzoic Acid.



$$COOHC_6H_4-N=N-C_6H_3\begin{matrix}/COOH\\ \backslash N(CH_3)_2\end{matrix}\ [49].$$

By action of m-diazobenzoic acid on m-dimethylamidobenzoic acid.

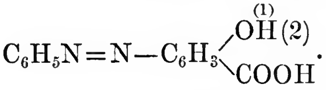
Azo-δ-diamidobenzoic Acid-p-benzenesulphonic Acid [9].



$$HSO_3-C_6H_4-N=N-C_6H_2\begin{matrix}/(NH_2)_2\\ \backslash COOH\end{matrix}.$$

Is prepared by action of p-diazobenzenesulphonic acid on δ-diamidobenzoic acid.

Azobenzenesalicylic Acid [52].



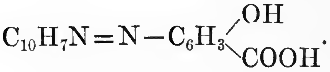
$$C_6H_5N=N-C_6H_3\left\langle\begin{matrix}\overset{(1)}{OH}(2)\\ COOH\end{matrix}\right. .$$

From diazobenzene and salicylic acid.

Monosulphonic Acid.

From p-diazobenzenesulphonic acid and salicylic acid [36].

Azonaphthalene-salicylic Acid [53].



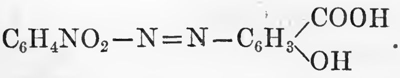
$$C_{10}H_7N=N-C_6H_3\left\langle\begin{matrix}OH\\ COOH\end{matrix}\right. .$$

From *a*-diazonaphthalene and salicylic acid. Dyestuffs have also been prepared from salicylsulphonic acid and diazo-compounds [54]. Meta- and para-oxybenzoic acids [36], as well as oxynaphthoic acids [55], give colouring-matters with diazo-compounds.

The dyes prepared from salicylic acid mostly possess the property of dyeing on alumina, iron, and chromium mordants, in a similar manner to alizarin.

This property, which is not met with in the meta- and paraoxy-derivatives, seems to be connected with the ortho position, as in the quinoneoxime dyes.

These mordant-dyeing properties are found in a much higher degree in the bodies obtained by action of nitrodiazo-compounds on salicylic acid (Germ. Pat. 44170, 16 Nov., 1887). The dyestuff from metanitrodiazobenzene and salicylic acid comes into commerce as Alizarin Yellow G, and produces a fine yellow lake with chromium oxide. The pure dyestuff crystallizes from alcohol in light yellow needles. M.P. about 230°. Its constitution may be expressed by the formula:—



$$C_6H_4NO_2-N=N-C_6H_3\left\langle\begin{matrix}COOH\\ OH\end{matrix}\right. .$$

It has been used to a certain extent in calico-printing as a substitute for Persian-berry extract and fustic extract. An isomeric compound from paranitrodiazobenzene is known as Alizarin Yellow R and gives more orange shades in dyeing.

These compounds are also useful in wool-dyeing. The dyeing process is simple, as owing to the stability of these compounds the mordanting with bichromate and the dyeing may be effected in one bath. α-oxynaphthoic acid combines with nitrodiazo-compounds, producing brown dyestuffs which possess the property, like the above, of dyeing on mordants.

V. TETRAZO- OR DISAZO-DYESTUFFS.

These bodies differ from the simple azo-compounds by containing the azo-group $-N{=}N-$ more than once in the molecule.

According to their method of formation and constitution, these compounds may be divided into different classes. The first of these classes, the type of which is phenolbidiazobenzene discovered by Griess, contain the two azo-groups and the auxochrome amido- or hydroxyl groups in one benzene nucleus. These compounds are obtained by the action of diazo-compounds on oxy- or amido-azo-compounds.

A second class contains only the azo-groups in one ring, while the auxochrome is in another. They may be prepared by acting upon amines or phenols with diazoazo-compounds (from amido-azo-bodies), or by diazotisation of diamines and subsequent combination with amines or phenols [43, 46].

A third class of tetrazo-dyestuffs includes those prepared from benzidine and its analogues. These contain two azo-groups in two different rings, which are linked to each other. Tertiary and quaternary azo-compounds, *i. e.*, those containing three and four azo-groups, have also been obtained.

Phenoldisazobenzene (*Phenolbidiazobenzene*) [28, 56].

$$C_6H_5N{=}N-C_6H_3OH-N{=}N-C_6H_5.$$

Is prepared by treating diazobenzene nitrate with carbonate of barium, or by the action of the former on oxyazobenzene.

It forms brown leaflets, M.P. 131°. A homologue, M.P. 110°, may be obtained from paradiazotoluene and oxyazobenzene [56].

Resorcindisazobenzene [46].

$$C_6H_5-N_2-C_6H_2(OH)_2-N_2-C_6H_5.$$

Two isomeric compounds are formed by the action of diazobenzene chloride on metadioxyazobenzene.

α. Soluble in alkalies, M.P. 215°.
β. Insoluble in alkalies, M.P. 222°.

p-diazotoluene reacts with m-dioxyazobenzene, three isomeric resorcindisazotoluenebenzenes being formed [46].

$$\text{Soluble in alkalies} \begin{cases} \alpha. \ \text{M.P. } 196^\circ. \\ \alpha_1. \ \text{M.P. } 241^\circ. \end{cases}$$

$$\text{Insoluble in alkalies} \quad \beta. \ \text{M.P. } 198^\circ.$$

Various disazo-compounds of this class may be obtained from azotolueneresorcin (from p-diazotoluene and resorcin) by action of diazobenzene and diazotoluene [46].

Amido-derivatives are produced by action of diazo-compounds on unsymmetrical diamidoazobenzene (chrysoïdine) and its homologues.

For example, chrysoïdine and diazobenzene chloride react to form azobenzenephenylenediaminebenzene [57]. M.P. 250°.

$$C_6H_5-N=N-C_6H_2(OH_2)_2-N=N-C_6H_5.$$

Homologues and carbonic acids of these bodies have also been prepared [57, 58].

AZO-DYES FROM AMIDOAZO-COMPOUNDS.

Amidoazo-compounds, of which the simplest representative is amidoazobenzene, are converted into the corresponding diazoazo-compounds, which latter, like simple diazo-compounds, react with amines and phenols, azo-dyes being formed. Amidoazosulphonic acids behave in the same way.

Benzenetetrazobenzenephenol (*Tetrazobenzenephenol*) [59].

$$C_6H_5-N=\overset{1}{N}-C_6H_4-\overset{4}{N}=\overset{1}{N}-C_6H_4O\overset{(4)}{H}.$$

Is formed by interaction of diazoazobenzene and phenol. It may be regarded as the simplest representative of this class.

Benzenedisazobenzene-β-naphthol [60].

$$C_6H_5-N=N-C_6H_4-N=N-C_{10}H_6\overset{\beta}{O}H.$$

(*Tetrazobenzene-β-naphthol.*)

From diazoazobenzene and β-naphthol. Forms a brick-red powder or brown leaflets with a green reflex. It is insoluble in alkalies, sparingly soluble in alcohol, easily in hot glacial acetic acid. It gives a green solution with concentrated sulphuric acid.

The sulphonic acids of this compound come into commerce as Biebrich and Croceïn scarlets, according to the position of the sulpho-group.

Monosulphonic Acid [60].

$$H\overset{(1)}{S}O_3C_6H_4\overset{(4)}{N}=\overset{(1)}{N}-C_6H_4\overset{(4)}{N}=N-C_{10}H_6\overset{\beta}{O}H.$$

From diazoazobenzenemonosulphonic acid and β-naphthol. The sodium salt forms red needles or an amorphous red powder which is sparingly soluble in cold water, more easily in hot water. The hot aqueous solution on cooling solidifies to a gelatinous mass. The calcium and barium salts are insoluble.

Disulphonic Acids.

A. $HSO_3C_6H_4N=N-C_6H_3HSO_3N=N-C_{10}H_6O\overset{\beta}{H}$ [60].

(BIEBRICH SCARLET.)

From diazoazobenzenedisulphonic acids and β-naphthol.

The sodium salt is easily soluble, and forms a thick syrup with a small quantity of water, becoming crystalline on long standing. It may be crystallized from dilute alcohol in red needles. The calcium and barium salts are insoluble.

Commercial Biebrich scarlet is generally this disulphonic acid, sometimes it contains the monosulphonic acid also. Both give a green solution with concentrated sulphuric acid. The shade obtained on wool and silk is a beautiful cochineal scarlet.

B. $HSO_3-C_6H_4-N=N-C_6H_4N=N-C_{10}H_5O\overset{\beta}{H}\,.\,HSO_3.$

The isomeric monosulphonic acids of β-naphthol react with diazobenzenesulphonic acid, producing dyes which, however, differ greatly according to the position of the sulpho-group. Schaeffer's β-acid gives dyes of a bluish shade and of little value, while the α-acid gives dyestuffs the shade of which is much superior to that of Biebrich scarlet.

This body [61] is known as Croceïn Scarlet 3B, and although not producing fast shades is used in cotton-dyeing. Croceïn Scarlet 7 B is a dyestuff of somewhat bluer shade, and is obtained from orthoamidoazotoluenesulphonic acid in the same manner. The tetrazo-dyes prepared from β-naphthol-α-sulphonic acid give soluble crystalline calcium salts, while those from the other acid give amorphous and insoluble calcium salts.

The G-disulphonic acid behaves similarly to the α-acid, and its combination with diazoazobenzene, known as Brilliant Croceïn M (Cassella & Co.), is closely allied to Croceïn 3 B. All the naphthol azo-dyes derived from amidoazobenzene and its homologues give a characteristic reaction on reduction, which readily serves for their recognition. On warming the alkaline solution with zinc powder, only the naphthol or its sulphonic acid is split off; the amidoazo-compound being regenerated.

Another characteristic property of the compounds of this class is that they exhibit a peculiar behaviour towards strong sulphuric acid.

The sulphonic acids containing the sulpho-groups in the benzene rings only react like the non-sulphonated azo-compounds, giving a green colour with concentrated sulphuric acid; if the sulpho-groups are in the naphthalene ring, a violet colour is obtained; while, if both rings are sulphonated, the colour is pure blue. On warming the green solution of benzene-disazobenzene-β-naphthol in sulphuric acid, the colour gradually changes to blue, and the sulphonic acid formed is identical with the one from diazoazobenzenemonosulphonic acid and β-naphthol-β-monosulphonic acid.

α-naphthylamine reacts with diazoazobenzenedisulphonic acid to produce a brown dyestuff, which is known as Archil Brown, possessing, however, no great importance.

The combination of diazoazobenzenedisulphonic acid with paratolyl-β-naphthylamine is known as Wool-Black.

Azodibenzenephenylenediamine [57].

$$C_6H_5N=N-C_6H_4-N=NC_6H_3(NH_2)_2.$$

Is formed by action of diazoazobenzene chloride on metaphenylenediamine. It forms brownish-red needles, which melt at 185°, and are easily soluble in chloroform, benzene, ether, and alcohol.

Azodibenzenetoluylenediamine [57].

$$C_6H_5N{=}N{-}C_6H_4N{=}N{-}C_7H_5(NH_2)_2.$$

From diazoazobenzene chloride and metatoluylenediamine. Forms light brown needles. Sulphonic acids of this compound are formed by using diazoazobenzenesulphonic acids.

Azobenzeneazoparacresol [42].

$$C_6H_5N{=}N{-}C_6H_4N{=}NC_6H_3{\substack{CH_3\\OH}}.$$

Is formed by action of diazoazobenzene chloride on paracresol. It forms brown needles, M.P. 160°, and dissolves in sulphuric acid with violet colour.

The diazoazonaphthalenes combine with sulphonic acids of the naphthols to form dyestuffs, some of which are used on a large scale.

Diazoazonaphthalenesulphonic acid, obtained by combination of β-naphthylaminesulphonic acid and α-naphthylamine, reacts with naphtholsulphonic acids, producing deep blue dyestuffs. One of these comes into commerce as Blue-black or Azo-black, and dyes wool a shade similar to that with nigrosine [68].

Other dyestuffs derived from amidoazo-compounds are comprised in the following table:—

Dyestuff.	*Diazotised Base.*	*Combined with*
Jet-Black R	Benzenedisulphonic acid azo-α-naphthylamine.	Phenyl-α-naphthylamine.
Fast Violet Bluish ..	β-toluenesulphonic acid azo-α-naphthylamine.	β-naphthol-β-sulphonic acid.
Diamond Black	Salicylic acid azo-α-naphthylamine.	α-naphthol-α-sulphonic acid.
Naphthylamine Black D.	Naphthalenedisulphonic acid azo-α-naphthylamine.	α-naphthylamine.
Brilliant Black......	Amidoazonaphthalenedisulphonic acid.	β-naptholdisulphonic acid R.

Meldola introduced a general method for preparing disazo-compounds [62]. Nitrodiazo-compounds are combined with phenols or amines; the nitro-group is then reduced, and the resulting amido-compound may be diazotised and again combined with an amine or a phenol. As an example of the method of procedure the following is cited.

Paranitrodiazobenzene combines with diphenylamine to produce:

$$NO_2-C_6H_4-N=N-C_6H_4NH-C_6H_5.$$

This body on reduction yields:

$$NH_2-C_6H_4-N=N-C_6H_4NH-C_6H_5.$$

This may be diazotised, and on combination with β-naphthol yields:

$$\beta\text{-}OH-C_{10}H_6-N=N-C_6H_4N=NC_6H_4NH-C_6H_5.$$

The dyestuffs obtained in this manner belong to the same series as those prepared with the diazo-compounds of paraphenylenediamine.

The nitroazo-compounds obtained by combination of nitrodiazo-compounds with primary amines may be diazotised and combined with phenols; resulting nitrodisazo-compounds on reduction yield amido-compounds, which, when again diazotised and combined with a phenol, yield tertiary azo-compounds, containing three azo-groups.

Paranitrodiazobenzene combines with α-naphthylamine, forming:

$$NO_2-C_6H_4N=N-C_{10}H_6NH_2\,\alpha.$$

This body, on diazotising and combining with β-naphthol, yields:

$$NO_2-C_6H_4-N=N-C_{10}H_6-N=N-C_{10}H_6OH\beta.$$

On reduction of the nitro-group, and treating with nitrous acid, a diazo-compound is obtained, which with β-naphthol yields a tertiary azo-compound:—

$$HOC_{10}H_6-N=N-C_6H_4N=N-C_{10}H_6-N=NC_{10}H_6OH\beta.$$

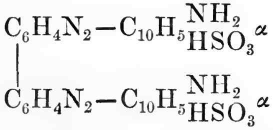
Numerous azo-compounds were prepared in an analogous manner, and for these reference must be made to the original article [62].

Azo-dyes from Benzidine and Analogous Bases.

The tetrazo-compounds obtained from benzidine and similar bases combine with phenols and amines to produce yellow, red, blue, and violet dyestuffs. These have attained considerable importance on account of their remarkable property of dyeing (in form of alkali salts) on unmordanted vegetable fibres.

The credit of this discovery belongs to P. Griess, who first remarked on it in his English patent (1884, No. 1099).

Tetrazodiphenyl combines with naphthionic acid, producing a dyestuff:—



$$\begin{array}{l} C_6H_4N_2-C_{10}H_5\begin{matrix}NH_2\\HSO_3\end{matrix}\alpha \\ | \\ C_6H_4N_2-C_{10}H_5\begin{matrix}NH_2\\HSO_3\end{matrix}\alpha \end{array}$$

which has considerable application under the name "Congo Red" [64].

The free sulphonic acid is blue, the salts are scarlet, and give the same shade on cotton. These shades, though fast to soap, are unfortunately turned blue by weak acids. This property is less marked in the dyestuff known as Benzopurpurine B. It is obtained [69] from tetrazoditolyl (obtained from o-tolidine and nitrous acid) and the β-naphthylaminesulphonic acid, obtained by Brönner from Schaeffer's β-naphtholsulphonic acid and ammonia.

It will be of interest, before entering into the consideration of these dyestuffs, to examine the constitution of the naphthylamine-sulphonic acids.

The sulphonic acids of α- and β-naphthylamine are used for production of azo-dyes in general, their principal application being in the manufacture of the direct-dyeing cotton-colours.

They are produced technically by two methods, either by direct sulphonation of the naphthylamines or by heating the naphthol-sulphonic acids with ammonia (*i.e.*, a compound yielding ammonia on heating).

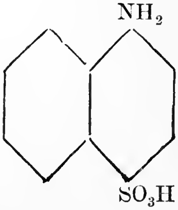
As the naphthylaminesulphonic acids are very numerous, only those of technical value will be considered here.

Only one of the sulphonic acids of α-naphthylamine, the so-called *naphthionic acid,* is of importance.

I. *Sulphonic Acids of α-naphthylamine.*

Naphthionic acid,

$C_{10}H_6{}^{NH_2}_{SO_3H}$,



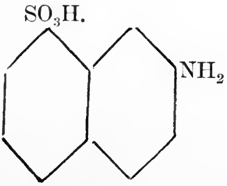
This acid is prepared by heating one part of α-naphthylamine with three to five parts of concentrated sulphuric acid at 100°, or by heating α-naphthylamine sulphate to 180°–200°.

II. *Sulphonic Acids of β-naphthylamine.*

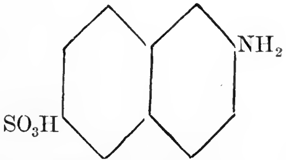
By the action of concentrated sulphuric acid on β-naphthylamine two monosulphonic acids are first formed, β-naphthylamine-α-sulphonic acid (corresponding to the croceïn acid from β-naphthol), and the β-naphthylamine-γ-sulphonic acid.

At a higher temperature two other acids are formed, the β-naphthylamine-β-sulphonic acid (Brönner's acid corresponding to the Schaeffer acid from β-naphthol), and β-naphthlyamine-F-sulphonic acid, corresponding to the F-acid from β-naphthol. The β- and F-acids are not products of direct sulphonation, but result from a molecular change in the α- and γ-acids, as both these acids, when heated with sulphuric acid, go over into a mixture of Brönner and F-acid. This mixture was termed δ-acid, and its discoverers, Bayer and Duisberg [76], and somewhat later Weinberg [77], showed that it could be split up into two acids—the Brönner and the F-acids. These β-naphthylaminesulphonic acids may also be produced by heating the corresponding naphtholsulphonic acids with ammonia (*i. e.*, a compound yielding ammonia on heating). In this manner the croceïn acid yields β-napthylamine-α-sulphonic acid, Schaeffer's acid yields β-naphthylamine-β-sulphonic acid, and the F-acid of Cassella yields the corresponding β-naphthylamine F-acid.

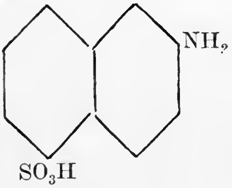
As yet the β-naphtholsulphonic acid corresponding to β-naphthylamine-γ-sulphonic acid has not been isolated from the acids formed in sulphonating β-naphthol. The constitutions of the acids, according to the most recent researches, may be graphically demonstrated by the following formulæ :—



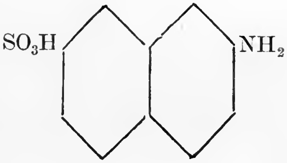
α-acid.



β-acid (Brönner)



γ-acid.



F-acid.

Of these sulphonic acids the β- and F-acids produce fine red dyestuffs with tetrazo-compounds, while the α- and γ-acids give worthless yellow ones.

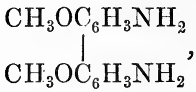
As has already been stated, the β-acid is used in the manufacture of Benzopurpurine B, and the F-acid serves, in combination with o-tetrazoditolyl, for production of a sparingly soluble, bluish-red dyestuff, known as Diamine-red 3 B.

If a mixture of both acids (*i. e.* the so-called δ-acid) is used, a fine mixed dyestuff is produced, which contains one molecule of each acid linked to the benzene chains of the ditolyl. This body forms the principal constituent of the dyestuff known as Delta-Purpurine 5 B. Mixed dyestuffs of this class are easily obtained, on account of a peculiar property of the tetrazo-compounds. The diazo-groups do not react simultaneously with the amine or phenol. The second diazo-group combines with some difficulty, and indeed the action is frequently aided by warming. Some of these dyestuffs are commercial products.

β-naphtholdisulphonic acid (R-acid) and α-naphthol-α-sulphonic acid both combine with tetrazodiphenyl and tetrazoditolyl, forming blue dyestuffs, which dye directly on unmordanted cotton.

The dyestuff from tetrazoditolyl and α-naphthol-α-sulphonic acid is known as Azo-blue, and produces reddish-blue shades on cotton, which are, however, fugitive to light [63].

A more stable dyestuff, which possesses at the same time a purer shade, is obtained from dimethoxylbenzidine,



$$\begin{array}{c} CH_3OC_6H_3NH_2 \\ | \\ CH_3OC_6H_3NH_2 \end{array},$$

and α-naphthol-α-sulphonic acid. It comes into commerce as Benzazurine [70].

The combination of tetrazodiphenyl and salicylic acid is known as Chrysamine [66]. It produces on cotton a somewhat sad yellow, and serves principally for production of the cream shades used as groundwork in calico-printing.

Tetrazostilbene (obtained by reduction of azoxystilbene and diazotisation of the resulting diamidostilbene) and its sulphonic acids yield numerous dyestuffs, some of which are capable of industrial application. Hessian Yellow, for example, is obtained by combining tetrazostilbenedisulphonic acid with salicylic acid.

The dyestuffs of this class have the property of acting to a certain extent as mordants for basic dyestuffs, and cotton dyed with them acts with basic dyestuffs as if prepared with tannic acid. Frequent application of this property is made in practice. For instance, methylene blue, green, &c., may be dyed on a blue azo-dyestuff, and in this manner the shades may be modified at will.

The following Table comprises the principal direct dyes at present in the market:—

Dyestuff.	*Diazotised Base.*	*Combined with*
Chrysamine G	Benzidine.	2 mols. salicylic acid.
Benzo-Orange G R	”	1 mol. salicylic acid. 1 mol. naphthionic acid.
Congo Yellow Paste	”	1 mol. sulphanilic acid. 1 mol. phenol.
Congo Red	”	2 mols. naphthionic acid.
Congo Corinth	”	1 mol. naphthionic acid. 1 mol. α-naphtholsulphonic acid N.W.
Brilliant Congo G	”	1 mol. β-naphthylamine-disulphonic acid R. 1 mol. β-naphthylamine-monosulphonic acid B.
Deltapurpurine G	”	2 mols. β-naphthylamine-δ-monosulphonic acid.
Azo-orseilline	”	2 mols. α-naphtholmonosulphonic acid N.W.
Benzidine Blue	”	2 mols. β-naphtholdisulphonic acid R.
Bordeaux Extra Congo Violet	”	2 mols. β-naphtholmonosulphonic acid B.
Diamine Black R	”	2 mols. amidonaphtholsulphonic acid prepared from β-naphthylamine-γ-disulphonic acid by melting with alkali.
Diamine Fast Red	”	1 mol. γ-amidonaphtholsulphonic acid. 1 mol. salicylic acid.
Diamine Violet N	”	2 mols. γ-amidonaphtholsulphonic acid.
Chrysamine R	Orthotolidine.	2 mols. salicylic acid.
Congo Red 4 R	”	1 mol. naphthionic acid. 1 mol. resorcin.
Congo Corinth B	”	1 mol. naphthionic acid. 1 mol. α-naphtholsulphonic acid N.W.
Brilliant Congo R	”	1 mol. β-naphthylamine-sulphonic acid B. 1 mol. β-naphthylamine-disulphonic acid R.
Benzopurpurine B	”	2 mols. β-naphthylamine-monosulphonic acid B.
Benzopurpurine 4 B	”	2 mols. naphthionic acid.
Benzopurpurine 6 B	”	2 mols. naphthylamine-monosulphonic acid (Laurent).
Delta-Purpurine 5 B	”	1 mol. β-naphthylamine-δ-monosulphonic acid. 1 mol. β-naphthylamine-monosulphonic acid B.

TABLE (*continued*).

Dyestuff.	*Diazotised Base.*	*Combined with*
Delta-Purpurine 7 B. .	Orthotolidine.	2 mols. β-naphthylamine-δ-monosulphonic acid.
Diamine Red 3 B. . . .		
Rosazurine B	”	2 mols. methyl-β-naphthylamine-δ-monosulphonic acid.
Rosazurine G	”	1 mol. methyl-β-naphthylamine-δ-monosulphonic acid. 1 mol. β-naphthylamine-δ-monosulphonic acid.
Azo-Blue	”	2 mols. α-naphtholsulphonic acid N.W.
Toluylene Orange G . .	”	1 mol. cresotic acid. 1 mol. metatoluylenediaminesulphonic acid.
Toluylene Orange R. .	”	2 mols. metatoluylenediaminesulphonic acid.
Brilliant Purpurine . .	”	1 mol. β-naphthylaminedisulphonic acid R. 1 mol. naphthionic acid.
Direct Red	Diamidophenyltolyl.	2 mols. naphthionic acid.
Cotton Red	Orthometatolidine.	2 mols. naphthionic acid.
Sulphonazurine	Benzidinesulphone disulphonic acid.	2 mols. phenyl-β-naphthylamine.
Rosazurine BB	Benzidinesulphone.	2 mols. naphthionic acid.
Diamine Red NO. . . .	Ethoxybenzidine.	1 mol. β-naphthylaminesulphonic acid B. 1 mol. β-naphthylaminesulphonic acid F.
Diamine Yellow N . .	”	1 mol. salicylic acid. 1 mol phenol. The product is then ethylated.
Diamine Blue B	”	1 mol. β-naphthol-δ-disulphonic acid. 1 mol. α-naphthol-α-sulphonic acid.
Diamine Blue 3 R . .	”	2 mols. α-naphthol-α-sulphonic acid.
Diamine Black B. . . .	”	2 mols. γ-amidonaphtholmonosulphonic acid.
Diamine Blue-Black E	”	1 mol. β-naphthol-δ-disulphonic acid. 1 mol. γ-amidonaphtholsulphonic acid.
Benzopurpurine 10 B	Dianisidine.	2 mols. naphthionic acid.
Rosazurine	”	2 mols. β-naphthylaminesulphonic acid B.
Benzoazurine G	”	2 mols. α-naphtholsulphonic acid N.W.

TABLE (*continued*).

Dyestuff.	*Diazotised Base.*	*Combined with*
Benzoazurine 3 G....	Dianisidine.	2 mols. α-naphthylamine-sulphonic acid (Cleve).
Brilliant Azurine 5 G	"	2 mols. dioxynaphthalene-monosulphonic acid from Schollkopf's acid.
Azo-Violet	"	1 mol. naphthionic acid. 1 mol. α-naphtholsulphonic acid N.W.
Heliotrope	"	2 mols. methyl-β-naphthylamine-δ-sulphonic acid.
Hessian Yellow	Diamidostilbenedisulphonic acid.	2 mols. salicylic acid.
Brilliant Yellow	Diamidostilbenedisulphonic acid.	2 mols. phenol.
Chrysophenine	Ethylation of	Brilliant Yellow.
Hessian Purple N....	Diamidostilbenedisulphonic acid.	2 mols. β-naphthylamine.
Hessian Violet......	Diamidostilbenedisulphonic acid.	1 mol. α-naphthylamine. 1 mol. β-naphthol.
Carbazol Yellow	Diamidocarbazol.	2 mols. salicylic acid.
Naphthylene Red ..	1·5 naphthylenediamine.	2 mols. naphthionic acid.
Salmon Red	Diamido-diphenylene.	2 mols. naphthionic acid.
Cotton Yellow	"	2 mols. salicylic acid.
Saint Denis Red	Diamido-azoxytoluene.	2 mols. naphtholsulphonic acid N.W.
Benzo-Brown B	Triamido-azobenzene.	Naphthionic acid.
Benzo-Blue-Black G	Benzidinedisulphonic acid disazo-α-naphthylamine.	2 mols. α-naphtholsulphonic acid N.W.
Benzo-Blue-Black R	Tolidine disazo-α-naphthylamine.	2 mols. α-naphtholsulphonic acid N.W.
Benzo-Black........	Benzidine disazo-salicylic acid α-naphthylamine.	2 mols. α-naphtholsulphonic acid N.W.

The property possessed by the above dyestuffs of becoming fixed on cotton from an alkaline bath (in form of their salts) is not, as has been supposed, peculiar to the derivatives of benzidine and its analogues. This characteristic is far more widely distributed, and has only been overlooked. Nearly all tetrazo-compounds may be fixed to a slight extent on cotton, and the dyestuffs obtained from paraphenylenediamine are almost as capable in this respect as the benzidine derivatives.

Azarin S [67].

The sodium bisulphite compound of an azo-dyestuff, prepared by combining dichlordiazophenol with β-naphthol, comes into commerce under the above designation.

This azo-dyestuff, which is insoluble, has a fine red colour, and possesses the property of forming a lake with alumina. By treatment with sodium bisulphite this body, like all azo-dyestuffs, yields an unstable sulphonic acid, which is only slightly coloured. If this compound is printed with aluminium acetate, and steamed, the sulphonic acid is decomposed, and the dyestuff combines with the alumina to a firmly adhering lake.

Azarin finds its principal application in calico-printing, and produces a fine red which, though fast to washing, is not sufficiently fast to light to compete with alizarin.

Another azarin is obtained by combination of diazotised diamidooxysulphobenzide (phenolsulphone) with β-naphthol. It is also applied in form of its bisulphite compound.

Sun-Yellow.

Another dyestuff closely related to the azo-compounds is a derivative of the so-called azoxystilbene. Its sulphonic acids dye cotton directly from an acid bath.

This yellow dyestuff is obtained by heating paranitrotolueneorthosulphonic acid with alkalies. It yields diamidostilbenesulphonic acid on reduction, but whether it is azoxystilbene or whether a ring-formation between the methane-group and the azo-chain has taken place is doubtful [78, 79].

The compound in question is known as Sun-Yellow.

Thiotoluidines (PRIMULINE) [80, 81].

By action of sulphur on paratoluidine, Merz and Weith obtained a base called thiotoluidine $(C_6H_3CH_3NH_2)_2S$, M.P. 103°. This reaction takes place at 140°; and if a higher proportion of sulphur and a more elevated temperature be employed, two new thiobases are formed, one of which is known as dehydrothiotoluidine

$C_{14}H_{12}N_2S$, and the other is the mother-substance of primuline. The salts of the sulphonic acid of the latter come into commerce as Primuline, Polychromine, &c. Primuline dyes unmordanted cotton directly from an alkaline bath, but its principal application is in connection with the so-called developers. This depends on the fact that primuline contains an amido-group capable of being diazotised on the fibre. This was introduced technically by Green as a method of producing insoluble azo-dyes direct on the fibre, the goods dyed with primuline being diazotised in a slightly acid bath with sodium nitrite, and then passed into the various yellow, red, &c. developers, which consist of certain amines and phenols in suitable solvents.

Erica.

Metaxylidine gives similar compounds if treated with sulphur. One of these, M.P. 107°, possesses one amido-group capable of being diazotised, and certain of the azo-dyes prepared with it form the various brands of Erica. These dyestuffs have the remarkable property of dyeing cotton from a bath containing sulphate of soda, producing pleasing pink shades of considerable fastness.

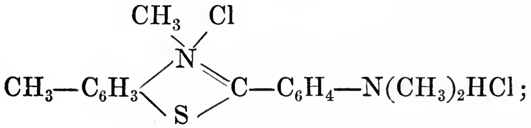
Erica B is the result of the combination of dehydrothiometaxylidine with α-naphthol-ϵ-disulphonic acid.

Thioflavine.

The Thioflavines, although not azo-dyes, are closely related to Primuline, and may therefore be described here.

By action of methyl chloride on dehydrothiotoluidine from the primuline melt, two compounds are formed, one of which comes into commerce in the form of its hydrochloride as Thioflavine T. It is a basic dyestuff, producing fine greenish shades of yellow. The second product of the reaction, which is separated from the previous one by means of its sparing solubility in dilute hydrochloric acid, yields on treatment with fuming sulphuric acid a sulphonic acid, a salt of which is sold under the name of Thioflavine S. It is a substantive dyestuff applied to cotton from an alkaline bath.

Thioflavine T is a dimethyldehydrothiotoluidine-methyl chloride of the formula—



and Thioflavine S is a sodium salt of dimethyldehydrothiotoluidinesulphonic acid, $C_{16}H_{15}N_2S_2O_3Na$.

DIRECT PRODUCTION OF AZO-DYES ON THE FIBRE.

Azo-dyes prepared by interaction of a diazo-compound and a phenol are insoluble in water, and therefore of no practical value. For this reason a sulpho-group is introduced (see p. 34), and this produces the solubility necessary for their application in ordinary dyeing processes. These sulphonated azo-dyes have a considerable affinity for wool and silk, but (with the exception of those of the tetrazo-series) are not easily fixed on cotton. Cotton may be dyed with certain azo-dyes of the Croceïn series, but the shades produced are not fast to washing.

The ease with which the combination of a diazo-compound and a phenol takes place, and the purity of the resulting product, doubtless led to the idea that insoluble azo-dyes might be produced by direct precipitation on vegetable fibres.

Messrs. Holliday were the first to make a practical application of the diazo-reaction in this direction, and in 1880 they patented processes whereby azo-dyes might be produced on vegetable fibres. Three alternative methods are prescribed :—

I. The goods are impregnated with an alkaline solution of a phenol, and the colour produced by passage through a solution of a diazo-compound.
II. The above process is reversed, the diazo-solution being applied first.
III. The goods are impregnated with a mixture of diazo-compound and phenol, and the colour developed by passage through alkali.

Grässler, in the same year, brought out a process whereby the use of acid to develop the nitrous acid necessary for diazotisation is avoided. A mixture of an amine, sodium nitrite, ammonium chloride, and a phenol is thickened, and the goods impregnated or printed with the mixture, and the colour developed by drying and steaming. A shade closely approaching Turkey red is obtained by using a mixture of xylidine and β-naphthol.

A process which has been used for silk-dyeing is similar to that of Messrs. Holliday. A diazo-compound in solution is neutralised by chalk, and a phenol (β-naphthol) obtained in a fine state of division by precipitation is added. On working the goods in this mixture, the colour is gradually developed and is fixed on the fibre.

Messrs. Meister, Lucius, and Brüning have recently modified the Holliday process, and adopt a method somewhat resembling the last described. It was found that the presence of free mineral acid in the solution of the diazo-compound is disadvantageous, and that brighter and more even shades are obtained if the free acid is neutralised by addition of chalk, or replaced by acetic acid, this being effected by addition of sodium acetate. The goods are worked first in the phenol dissolved in water in presence of two molecules of caustic soda, dried, passed into the prepared solution of the diazo-compound, and washed till the wash-waters are colourless.

In general the theoretical proportions indicated by equation are adhered to in the preparation of the diazo-solutions; certain bases, however, are not easily soluble, and are brought into commerce in pastes containing 25 per cent. of amine and the amount of nitrite necessary for diazotising. The diazo-solution is obtained by solution in the calculated amount of dilute hydrochloric acid. The red shades obtained by this process become duller on soaping, with the exception of those from the amidoazo-compounds. The shades obtained from amidoazo-compounds are also faster to light than those from simple amines. The shades obtained with β-naphthol are bright orange-yellow to red, those from α-naphthol having a brown tone. A shade approximating to Turkey red is obtained from β-naphthol and diazotised β-naphthylamine.

The above processes are purely mechanical, the goods being simply impregnated with the diazo-compound, or phenol. Another group of methods differs in an important respect—that the amine is first actually fixed, by dyeing, on the fibre. It has already been mentioned that primuline (an amine) may be fixed on cotton, diazotised on the fibre, and new azo-colours produced by passage of the goods through developers, *i. e.* solutions of amines or phenols capable of combining with the diazo-compound of primuline. It is evident that this method must be more advantageous than those in which the diazo-compound is in mere mechanical incorporation with the fibre, shades produced by the latter process being more liable to rub.

Of late a new class of direct-dyeing cotton-colours has been introduced. These contain one or more free amido-groups capable of diazotisation, and are therefore suitable for direct production of azo-dyes on the fibre. Amongst these dyestuffs are Diamine Blue-Black E, Diamine Black B and R (see Table). These dyestuffs are combinations of diazotised bases of the Benzidine series with one or two molecules of an amidonaphtholsulphonic acid, and these amido-groups, in the naphthol compound remaining intact, may subsequently be diazotised.

Cotton is dyed in a bath containing Glauber's salt and a little soap or soda, and the shades produced vary from dark blue to bluish black, about 6 per cent. of dyestuff being necessary to produce a maximum effect. The diazotising is effected by a bath of sodium nitrite acidified with hydrochloric acid. The developing-bath varies according to the shade required. Resorcin, β-naphthol, and phenylenediamine produce blacks of various shades; blues are obtained with naphthylamine ether; and mixtures of these developers produce blacks of every conceivable shade.

In all these processes depending on the use of diazo-compounds the principal point is to work as cold as possible. Diazo-compounds decompose with a slight elevation of temperature, and are unstable at ordinary temperatures, and therefore it is necessary to work as expeditiously as possible. In the Holliday and allied processes, where a diazo-compound is used in solution, ice is frequently necessary for its preservation; where the diazo-compound is produced on the fibre, this is not of such great moment.

CHAPTER III.

OXYQUINONES AND QUINONEOXIMES.

THE quinones belong to the most powerful class of chromogens, and this is equally true of both the para- and orthoquinones. They yield actual dyestuffs by introduction of auxochromic groups. The oxyquinones possess a specially marked dyestuff-character, as the quinone group belongs to the acid-forming chromophors, and the hydroxyl group introduced develops powerful acid properties.

All the oxyquinones are coloured and form salts of still darker colour. Most of them may be fixed directly on animal fibres, but the shades obtained are weak and without value.

The true character of a number of these bodies only appears in their combinations with metallic oxides; in other words, the oxyquinones belong to the class of "mordant-dyeing" colouring-matters. They are especially distinguished by the beauty and fastness of their metallic lakes.

An interesting property in connection with these bodies is that only such oxyquinones as have one hydroxyl group in the ortho-position to the quinone-oxygen possess this power of dyeing on mordants, and that in general it is necessary to have simultaneously two hydroxyl-groups in the ortho-position to each other [32, 33].

The rest of the oxyquinones form coloured metallic salts which are often insoluble, but which do not possess the essential property of adhering to fibre.

The oxyquinones of the benzene series contain at least one hydroxyl group besides the quinone-oxygen, and so far as they have been examined are capable of dyeing on mordants in a greater or less degree. Tetroxyquinones, rhodizonic acid (dioxydiquinoyl) and nitranilic acid (dinitrodioxyquinone) have great power in this direction, while it is present to only a slight extent in dioxyquinone and chlor- and bromanilic acids.

The tinctorial power of these bodies is, however, slight, and a dyestuff of sufficient intensity and stability is only reached in the naphthalene series. This is naphthazarin, a dioxyquinone of unknown constitution.

The quinoneoximes closely resemble the oxyquinones in their properties. Only compounds derived from orthoquinones are capable of fixation on mordants. Mono- or dioximes are formed by substitution of one or both quinone-oxygen atoms in an orthoquinone by the isonitroso-group NOH.

Both may be dyed on metallic mordants, especially on iron or cobalt oxide. The mono-oximes, however, are more useful in this respect, and have for some time been applied technically.

Naphthazarin (Dioxynaphthoquinone).

$C_{10}H_4O_2(OH)_2$.

This compound was discovered by Roussin in the year 1861, and for some time was thought to be alizarin. It is obtained by heating α-dinitronaphthalene with concentrated sulphuric acid, fragments of zinc being added to the hot solution. It sublimes in brown needles, with a cantharides lustre. It is sparingly soluble in water, easily in alcohol and glacial acetic acid, with a red colour. It forms a blue solution with alkalies and a red one with strong sulphuric acid. It combines with sodium bisulphite, and the compound formed dissolves readily in water. Naphthazarin dyes excellently on mordanted fibres, giving a violet on alumina and a grey on chromic oxide.

Naphthazarin has recently been introduced into commerce as Alizarin Black. The commercial product is the bisulphite compound, and finds its principal application in printing. For this purpose it is mixed with chromium acetate. On steaming the bisulphite compound is decomposed, and the naphthazarin combines with the chromic oxide to form a firmly adhering lake.

ANTHRAQUINONE DYESTUFFS.

Anthraquinone itself has only a slight yellow colour, while all its hydroxyl derivatives have a more or less marked colour, generally orange-yellow to red. The solutions of the alkali-salts are generally red or violet. Certain of these bodies possess affinity for animal fibres, and may be fixed like acid colours, but the shades produced have no practical value.

The utility of these dyestuffs depends solely on their capability of forming insoluble lakes with metallic oxides. These lakes may be firmly fixed on textile fibres, their colour varying according to the nature of the metal. Indeed the metallic compounds of these bodies may be looked upon as so many different dyestuffs.

Of the numerous hydroxyl derivatives of anthraquinone, only those which have two hydroxyl-groups in the 1, 2-position to the carbonyl-group of anthraquinone are capable of dyeing upon mordants. In other words, only alizarin and its derivatives possess this property. As the number of anthraquinone derivatives is very large, we must necessarily confine ourselves to those of technical value.

Alizarin [2, 3].

$C_{14}H_8O_4$.

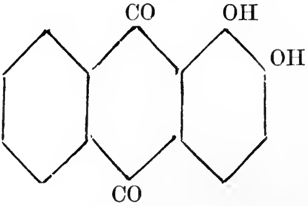
Alizarin is one of the few natural dyestuffs which have been prepared synthetically, and is probably the only one which is prepared artificially on the large scale. It occurs generally as a glucoside, ruberythric acid $C_{26}H_{28}O_{14}$ [1, 2] in madder, the root of *Rubia tinctorium*, and also in some other plants.

Ruberythric acid splits up by boiling with dilute acid, or by fermentation, glucose and alizarin being formed.

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

Alizarin crystallises in reddish-brown needles, which are almost insoluble in water, sparingly soluble in alcohol, more easily in hot glacial acetic acid, carbon disulphide, and glycerine. It melts at 289° to 290° C., and sublimes at a higher temperature in beautiful long red needles. It dissolves in alkalies with a violet colour, and the sparingly soluble acid salts may be precipitated from these solutions by carbonic acid. On oxidation with nitric acid it gives phthalic acid, and by heating with zinc powder anthracene is formed. With the oxides of aluminium, barium, calcium, iron, and most of the heavy metals it gives characteristic coloured insoluble lakes. The red alumina lake, the maroon chromium lake, and the violet-black iron lake are of importance in dyeing.

The hydroxyl-groups in alizarin are in the adjacent positions to one carbonyl-group of anthraquinone, and its constitution may be expressed by the following formula [4] :—



The hydroxyl-hydrogen atoms of alizarin may be replaced by alcohol and acid radicals. The alkyl derivatives are easily obtained by heating alizarin with the requisite alkyl iodide in presence of caustic alkali. Mono- and di-derivatives may be obtained in this manner [5, 6].

Acetic anhydride gives a diacetyl derivative, M.P. 160° C. [7]. Chlorine acts on alizarin, forming a monochloralizarin; with antimony pentachloride, dichlor- [8] and finally tetrachlor-alizarin may be obtained. Corresponding bromine derivatives have also been prepared [8, 9, 10].

On heating with ammonia in sealed tubes two isomeric alizarin amides (oxyamido-anthraquinones, $C_{14}H_6O_2(OH)NH_2$) are obtained. The principal product of the reaction is the meta-compound with a small quantity of the ortho.

Sulphonic acids of alizarin have also been prepared, and are met with in commerce under the name of Alizarin Red S.

Alizarin may be prepared artificially by fusing dibromanthraquinone, nitroanthraquinone, or anthraquinonesulphonic acid with potash or soda [3]; also by condensation of phthalic acid with pyrocatechin [4], and by reduction of rufigallic acid [13]. Alizarin has only been prepared on an industrial scale from anthraquinone, and the artificial product has practically displaced madder in the course of the last twenty years.

The synthesis of alizarin was first effected by Graebe and Liebermann in 1869. These chemists had already observed the formation of anthracene from natural alizarin by heating with zinc powder, and recognizing alizarin as a derivative of anthracene, attempted to convert anthracene into alizarin. This aim was accomplished by fusion of bibromanthraquinone with potash. In the same year Graebe, Liebermann, and Caro [14] discovered the formation of alizarin by melting anthraquinonesulphonic acid with caustic potash. This process, which is in use at the present day, was discovered almost simultaneously by W. H. Perkin [15].

Other processes have been proposed for the manufacture of alizarin, for instance by melting dichloranthraquinone or nitroanthraquinone [16] with caustic potash, but these processes have never attained commercial importance.

For a long time it was thought that the anthraquinonedisulphonic acids gave rise to the formation of alizarin, but this assumption was based on an error. The monosulphonic acid alone is capable of giving alizarin, while the disulphonic acids yield isopurpurin and flavopurpurin. This was already known to some technologists in 1871, but was first published by Perkin in 1876 [17].

The formation of alizarin from anthraquinonesulphonic acid does not appear to be due to any uniform reaction. On the one hand, oxyanthraquinone is formed and becomes oxidised in the alkaline melt to alizarin; on the other hand, oxyanthraquinonesulphonic acid is also a constituent of the melt, and yields alizarin by replacement of its sulpho-group by hydroxyl. Alizarinsulphonic acids are also often found in the alizarin melt. It is not improbable that these different reactions are due to the existence of several isomeric anthraquinonesulphonic acids.

For the manufacture of alizarin on a large scale a very pure anthraquinone is required, and this is generally prepared by oxidation of anthracene with sodium bichromate and dilute sulphuric acid. The anthracene is generally a 50-per-cent. product which has been converted into a soft powder by subliming with superheated steam. The oxidation takes place in lead-lined vessels in which the mixture is heated by direct steam. By employing a pure anthracene and a not too concentrated oxidation-mixture, the anthraquinone separates as soft grey powder, which is freed from acid by washing with water. The crude product is then dried, dissolved in concentrated sulphuric acid, and precipitated with water. A further purification is effected by sublimation with superheated steam.

For production of monosulphonic acid a somewhat concentrated fuming sulphuric acid (containing 30 to 40 per cent. anhydride) is required, and the sulphonation should take place at as low a temperature as possible.

The monosulphonic acid is separated from the disulphonic acids simultaneously formed by fractional crystallisation of the sodium salts. By saturating the acid mixture with soda, the salt of the monosulphonic acid separates first. At present the sulphonation is carried out so as to produce as much monosulphonic acid as possible with only a little disulphonic acid.

As has already been stated, the reaction in the melt proceeds in two directions, viz., a substitution of the sulpho-group by hydroxyl and a direct oxidation.

In the older processes this oxidation was effected by air, and if the supply of this was insufficient, took place at the cost of some of the materials. To prevent this a large surface of the melt was exposed to the air by melting in shallow pans.

This process has been abandoned for about ten years, and the atmospheric oxygen is dispensed with by adding an oxidising agent (potassium chlorate), and operating in closed vessels under pressure. This improvement is of great advantage, as the temperature is easily regulated, even if the melt contains much water; while in open vessels a certain concentration is necessary before the required temperature is reached. In place of the older melting process, the sulphonic acids are now heated with concentrated soda-lye under pressure.

The operation takes place in a horizontal cylindrical iron vessel fitted with a stirrer. Into this are introduced one part of anthraquinonemonosulphonate of soda, with about three parts of caustic soda and a certain amount of water and chlorate of potash. The mixture is then heated several days to 180°–200°.

The melt is then dissolved in water and the sodium compound decomposed by adding hydrochloric acid. The precipitate of alizarin is then well washed, and brought into commerce as a 10 to 20 per cent. paste. Its value may be ascertained by an estimation of the solid matter and ash, a dye-trial also being made.

Blue and yellow shades of alizarin are known; the former consists of pretty pure alizarin, while the latter contain both the trioxyanthraquinones isopurpurin and flavopurpurin. Alizarin may be fixed directly on wool, the shade produced being weak, and of the yellowish-red tone characteristic of free alizarin solutions. This shade has no value in dyeing, and the application of alizarin is solely in form of its brightly coloured aluminium, chromium, and iron lakes.

Most of the alizarin made is used in cotton-dyeing and printing, although a considerable amount is also used in wool-dyeing.

Alizarin gives entirely different shades with different metals. In dyeing and printing the beautiful red alumina lake and the violet-black iron lake are almost exclusively used. Sometimes the chromium lake is also applied.

In order to dye alizarin on cotton, the latter is impregnated with the necessary metallic oxide, and brought into a bath containing alizarin in a fine state of suspension, the bath being gradually heated to boiling; although alizarin is so slightly soluble in water, its solubility is sufficient to effect its combination with the metallic oxide on the fibre. For test-dyeing with alizarins printed calico is used. This calico contains stripes of alumina and iron and mixtures of these, printed in different degrees of strength, and on dyeing in an alizarin-bath various shades are obtained.

In printing, a mixture of alizarin paste and aluminium or iron acetate is used. On steaming, the acetate is decomposed, and the formation of the colour-lake takes place.

In alizarin-dyeing, a great number of purely empirical operations are common, especially in turkey-red dyeing. Brilliant scarlet tones of turkey-red can only be obtained on alumina and oil mordants. The oil formerly used was a very rancid olive-oil, "Huile tournante," but this has been entirely replaced by the so-called turkey-red oil. This product is a ricinoleate of ammonia, obtained by treating castor-oil with strong sulphuric acid, and neutralizing the separated fatty acid with ammonia. It is probable that the alumina forms double compounds with the fatty acids and with the alizarin, these compounds possessing a more brilliant colour than the simple alizarin lakes. The turkey-red process is very complicated, and comprises many operations which are not properly understood. For instance, treatment in a bath of cow-dung and other similar processes.

Wool is mordanted with alumina, for alizarin-dyeing, generally by boiling in a bath of alum tartar. Chromium mordants are also used in connection with alizarin for production of maroon shades.

The shades obtained with alizarin are very stable. They resist the action of soap and bleaching-powder, and are almost entirely unaffected by light.

Nitroalizarin [18, 19].

$C_{14}H_7(NO_2)O_4$.

Only the β-nitro-compound (of the constitution $\overset{(1)}{OH}\ \overset{(2)}{OH}\ \overset{(3)}{NO_2}$) possesses technical interest. It may be obtained by treating alizarin, suspended in toluene or nitrobenzene, with nitrous acid, or by cautious nitration of alizarin dissolved in glacial acetic acid with nitric acid.

Pure β-nitroalizarin forms orange-yellow needles, which melt at 244°, with partial decomposition [19]. It sublimes in yellow leaflets, undergoing partial decomposition. It dissolves in benzene and glacial acetic acid, and gives a purple-red solution with alkalies. The violet lime-lake is not decomposed by carbonic acid. (Distinction from alizarin.) It forms a diacetyl compound, M.P. 218° [19]. Nitroalizarin dyes orange shades on alumina mordants, and reddish-violet on iron mordants.

It comes into commerce in paste as Alizarin Orange, and is used in dyeing and printing, though its principal application is in the manufacture of Alizarin Blue.

TRIOXYANTHRAQUINONES.

$C_{14}H_5(OH)_3O_2$.

A. *Purpurin* [position 1, 2, 4].

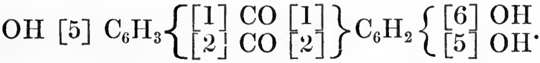
Purpurin occurs with alizarin in the madder root [20], probably also as glucoside. It may be obtained artificially from alizarin by heating with manganese dioxide and sulphuric acid [21], or arsenic acid; and also by melting an alizarinsulphonic acid (the so-called alizarin purpursulphonic acid) with potash [11].

Purpurin forms long orange-yellow needles which contain one molecule of water. It dissolves pretty readily in alcohol, ether, and benzene, and is also much more easily soluble in water than alizarin. It loses its water of crystallisation at 100°, and sublimes at a comparatively low temperature. M.P. 253°.

The alkaline solutions of purpurin are reddish violet, and rapidly become bleached on exposure to light and air. The presence of certain metallic oxides produces a characteristic effect on the absorption-spectrum of purpurin solutions, and these may serve for the detection of alumina and magnesia [22, 23]. Purpurin dissolves in boiling alum solution, forming a yellowish-red fluorescent solution, from which the purpurin separates on cooling. As alizarin is almost insoluble in alum solution, this method is used for the separation of these bodies. Although the alkaline solutions of purpurin are easily bleached by light, the alumina lake is perfectly stable against this agency.

On alumina mordants purpurin produces a beautiful scarlet red, much yellower in tone than that from alizarin, but its application is limited, as its price is much higher than that of isopurpurin.

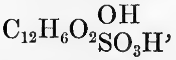
B. *Isopurpurin* (*Anthrapurpurin*) [24, 25, 26].



$$\mathrm{OH}\ [5]\ C_6H_3\left\{\begin{matrix}[1]\ \mathrm{CO}\ [1]\\ {[2]}\ \mathrm{CO}\ [2]\end{matrix}\right\}C_6H_2\left\{\begin{matrix}[6]\ \mathrm{OH}\\ {[5]}\ \mathrm{OH}\end{matrix}\right..$$

Isopurpurin is obtained by melting β-anthraquinonedisulphonic acid with caustic potash, an isomer of alizarin, isoanthraflavic acid, being formed as a bye-product [26].

In the first stage mono-oxyanthraquinonesulphonic acids,



$$C_{12}H_6O_2\begin{matrix}\mathrm{OH}\\ \mathrm{SO_3H}\end{matrix},$$

are formed, and these are oxidised to alizarinsulphonic acids, a small portion being converted into anthraflavic acids. These alizarinsulphonic acids yield the purpurins by exchange of a sulpho- for an hydroxyl group [42].

It forms orange needles, which are soluble in alcohol but insoluble in benzene. Its M.P. is above 330° [25]. It yields no phthalic acid on oxidation, and therefore probably contains the third OH-group in the second benzene ring. Isopurpurin is the principal constituent of the commercial alizarin for red. It dyes a fine scarlet red on alumina; its iron lake is greyish violet, and of little value.

C. *Flavopurpurin* [26, 27].

$$\mathrm{OH}\ [4]\ C_6H_3\left\{\begin{matrix}[1]\ \mathrm{CO}\ [1]\\ {[2]}\ \mathrm{CO}\ [2]\end{matrix}\right\}C_6H_2\left\{\begin{matrix}[6]\ \mathrm{OH}\\ {[5]}\ \mathrm{OH}\end{matrix}\right..$$

Flavopurpurin is obtained from α-anthraquinonedisulphonic acid; anthraflavic acid, an isomer of alizarin, is formed as a bye-product. It forms golden-yellow needles, easily soluble in alcohol, M.P. above 330° C. It dissolves with purple-red colour in caustic soda, and yellowish-red in ammonia and sodium carbonate.

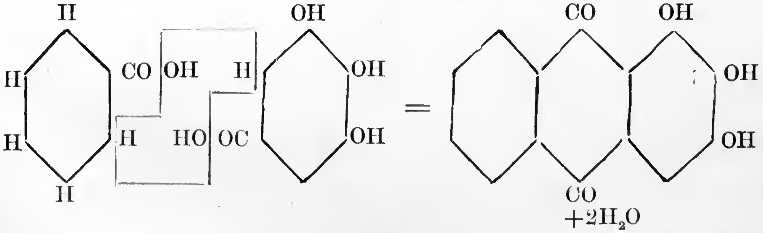
On alumina mordants it gives a red, which is still yellower than that with isopurpurin. Its principal application is in printing, while that of isopurpurin is in dyeing. Anthraflavic acid and isoanthraflavic acid sometimes occur in the commercial products. They are entirely valueless in dyeing, and are produced in badly conducted operations.

Like isopurpurin, flavopurpurin contains the third hydroxyl-group in the second benzene nucleus.

D. *Anthragallol* [41].

This trioxyanthraquinone is not prepared from anthracene, but is obtained by condensation of gallic acid with benzoic acid. In anthragallol the three hydroxyl-groups occupy adjacent positions [1 : 2 : 3].

It is prepared by heating equal molecules of benzoic acid and gallic acid with concentrated sulphuric acid. The following equation expresses the reaction which takes place :—

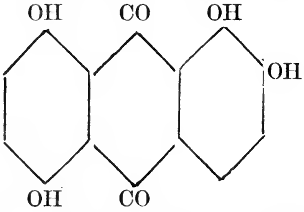


Anthragallol has a brown colour, and dyes brown shades on alumina or chromic oxide. The commercial Alizarin Brown is a mixture of anthragallol with more or less rufigallic acid.

The latter compound is hexaoxyanthraquinone, and is formed in a similar manner to anthragallol by condensation of gallic acid. It belongs to the mordant anthraquinone-derivatives.

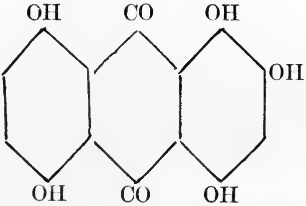
Alizarin Bordeaux and Alizarin Cyanine [38, 39].

On treating dry alizarin with a large quantity of sulphuric acid containing 70 per cent. anhydride, a peculiar ether of sulphuric acid is obtained, which on boiling with water splits up into a new dyestuff, "Alizarin Bordeaux," and sulphuric acid. This alizarin Bordeaux is a tetraoxyanthraquinone identical with quinalizarin:



This dyestuff produces fine Bordeaux shades on alumina mordants, and in colour-printing a blackish blue is obtained with a chromium mordant. On wool a deep claret with a violet tone may be obtained. Alizarin Bordeaux crystallises from nitrobenzene in fine red needles which have a metallic lustre. It may be distilled, undergoing only slight decomposition.

If alizarin Bordeaux be dissolved in concentrated sulphuric acid and treated with manganese peroxide or arsenic acid, oxidation takes place, a pentoxyanthraquinone being formed:—



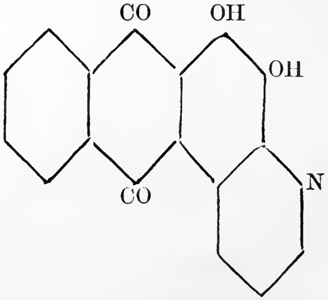
This body comes into commerce as Alizarin Cyanine R or as Alizarin Blue CR. Alizarin cyanine crystallises from glacial acetic acid in beautiful crystals, and dissolves in concentrated sulphuric acid with a blue colour and a fine red fluorescence. If dyed on cotton mordants with alumina, fine violet shades are produced, and chromium mordants give dark blues. In the preparation of alizarin cyanine R, a sulphuric ether is formed as intermediate product, and on treating with ammonia this body yields a dyestuff which differs from alizarin cyanine R inasmuch as it produces considerably greener shades. It is also a commercial product, and is sold under the name Alizarin Cyanine G. Analogous series of reactions may be carried out with the isomers and homologues of alizarin, for example, "Bordeaux" and "Cyanines" corresponding to those described above may be obtained from purpurin, anthrapurpurin, flavopurpurin, and anthragallol.

Alizarin Blue [28, 29, 30].

This dyestuff is prepared by heating β-nitroalizarin with glycerine and sulphuric acid. It is peculiar in so far that it possesses the lake-forming properties characteristic of the alizarin dyes, and is at the same time a weak base. Alizarin blue was discovered by Prud'homme [28], and the determination of its constitution by Graebe [29] led to the synthesis of quinoline by Skraup from glycerine, nitrobenzene, and aniline.

Alizarin blue has the composition $C_{17}H_9NO_4$, and stands in the same relation to alizarin as quinoline to benzene.

Its constitutional formula is as follows [29]:—



In the pure state (crystallised from benzene) it forms brownish-violet needles, insoluble in water and difficultly soluble in ether and alcohol. It melts at 270°, and sublimes, forming orange vapours. It dissolves in alkalies with a blue colour, an excess of alkali turning the solution green. Its salts with acids are of a reddish colour, and are decomposed by water.

On distillation with zinc powder it yields anthraquinoline, $C_{17}H_{11}N$ [29].

With chromium oxide, alizarin blue gives a stable indigo-blue lake.

It is chiefly applied in the form of its bisulphite compound, the latter being the principal constituent of the commercial Alizarin Blue S [31]. This is a reddish-brown compound and is decomposed on heating, alizarin blue separating. The bisulphite compound is printed with acetate of chromium; and, on steaming, the chromium lake of alizarin blue is fixed on the fibre. The bisulphite compound may be precipitated from its solutions by common salt, and comes into commerce as an easily soluble brown powder.

Alizarin Indigo-blue S, *Alizarin Green* S [40].

Alizarine blue may be oxidised by action of fuming sulphuric acid, the process being analogous to that used for the preparation of Alizarin Bordeaux. At 50° to 60° a dyestuff called Alizarin Blue-green is formed, and is best isolated in form of its bisulphite compound. It is a monosulphonic acid of mono-oxyalizarin blue.

If the mixture be heated to 120°, or if alizarin blue-green is heated with concentrated sulphuric acid to 120°, an intramolecular change takes place, a new mono-oxyalizarin blue monosulphonic acid being formed. This body is an article of commerce, and is known as Alizarin Green S.

If, finally, the temperature of the reaction between sulphuric acid and alizarin blue be raised to 200° to 210°, or if alizarin green is heated to the same temperature with concentrated sulphuric acid, a third dyestuff, Alizarin Indigo-blue, is obtained. This body is a trioxyalizarin-blue. The commercial products are pastes which contain the bisulphite compounds. The shades produced in dyeing are sufficiently indicated by the names, being a dull indigo-blue and a dull bluish green respectively. The best results are obtained with chromium mordants.

Styrogallol [36, 37].

$C_{16}H_8O_5$.

This compound is obtained by heating gallic acid with cinnamic acid in sulphuric acid solution to 55°. It forms light yellow needles. M.P. 350°. It is insoluble in water, and sparingly soluble in alcohol, glacial acetic acid, and aniline.

Its solution in alkalies is green, changing through violet to red on warming. It dissolves in strong sulphuric acid with a yellowish-red colour.

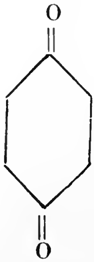
Styrogallol is probably an o-dioxyanthracoumarine. On warming with acetic anhydride a diacetyl derivative, M.P. 260°, is obtained.

On alumina mordants it dyes an orange-yellow shade, similar to alizarin orange, but owing to its high price has not been used practically.

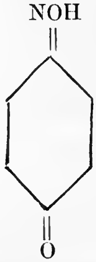
A dibrominated dioxy-β-methylcoumarine is known commercially as Anthracene Yellow.

QUINONEOXIMES.

These compounds are obtained by action of nitrous acid on phenols, and were formerly regarded as nitrosophenols; but this assumption has gradually been abandoned. They may also be obtained by action of hydroxylamine on quinones, and yield dioximes on further treatment with this reagent. It is therefore more probable that the nitrosophenols are really oximes of quinones, *i. e.*, quinones in which one oxygen atom is replaced by the divalent group = N—OH.



Quinone.



Quinoneoxime
(Nitrosophenol).

The quinoneoximes, like the quinones, are mostly yellow, but possess little tinctorial power. Certain oxime-derivatives of orthoquinones, however, like oxyquinones, are capable of combining with mordants (especially iron and cobalt), forming highly coloured lakes which may be fixed on textile fibres.

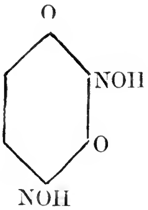
Some of this latter class of quinoneoximes are described in detail, as they have attained some importance as adjective dyestuffs.

Dinitrosoresorcin (*Diquinoyldioxime*) [32].

$C_6H_2O_2(NOH)_2$.

This compound is obtained by treating an aqueous solution of resorcin with nitrous acid (sodium nitrite and sulphuric acid). Dinitrosoresorcin crystallises from alcohol in yellowish-brown leaflets, which deflagrate at 115°. It is a pretty strong dibasic acid, and forms easily soluble salts with alkalies.

Its constitution is probably expressed by the following formula [33]:—

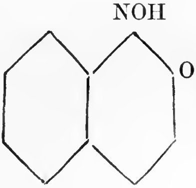


The iron lake of dinitrosoresorcin is green, and the latter produces green shades on cotton prepared with iron mordants. It has been used for some time in cotton-dyeing under the name "Fast Green."

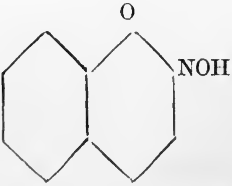
Naphthaquinoneoximes [34].

$C_{10}H_6O(NOH)$.

β-naphthaquinone yields two oximes, both of which are capable of dyeing on mordants, while this property is absent in the oxime of α-naphthaquinone (α-nitroso-α-naphthol),



α-nitroso-β-naphthol is obtained by action of nitrous acid on β-naphthol, while α-naphthol under similar treatment gives β-nitroso-α-naphthol,



along with some α-α-compound.

Both derivatives of β-naphthaquinone give intensely green lakes with ferric oxide, while their cobalt lake is dark red, being known in commerce as Gambine R and G respectively; but they are not of great importance.

The iron salt of a sulphonic acid of the α-β-compound comes into commerce as Naphthol Green [38, 39].

The sulphonic acid is prepared by acting on Schaeffer's acid with nitrous acid. The iron compound of this acid is soluble in water, and is fixed on animal fibres like the acid dyestuffs.

Naphthol green is used to some extent in wool-dyeing.

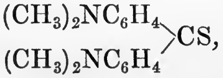
The dyestuff known as Dioxine is a nitroso-derivative of 1·8 dioxynaphthalene.

CHAPTER IV.

KETONEIMIDES AND HYDRAZIDES.

These bodies, certain of which have been used as dyestuffs, are derived from the simple ketones in the same manner as the quinone-imides and quinone-hydrazides from the diketones (quinones). Here, however, the chromophor occurs in an open carbon chain, and as it is only of a weak character, requires a salt-forming group to develop the properties of a dyestuff. The colour produced is always yellow.

It has already been remarked that the CO group, when it does not occur as a member of a closed carbon ring, cannot act as a chromophor, and only becomes one when the oxygen is replaced by sulphur or by a nitrogenous group. So far as the present state of knowledge reaches, all benzophenone derivatives are colourless. On the other hand, thiobenzophenone yields coloured derivatives. Tetramethyldiamidothiobenzophenone [3] :—

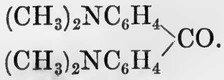


$$\left.\begin{matrix}(CH_3)_2NC_6H_4\\(CH_3)_2NC_6H_4\end{matrix}\right>CS,$$

for example, is intensely yellowish red, but is no dyestuff.

If the sulphur in this compound be replaced by the imide-group NH, auramine, the only representative of the ketoneimide dyestuffs known, is formed.

The starting-point for the manufacture of auramine is tetramethyldiamidobenzophenone,



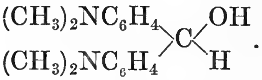
$$\left.\begin{matrix}(CH_3)_2NC_6H_4\\(CH_3)_2NC_6H_4\end{matrix}\right>CO.$$

This base was discovered by Michler [2] in 1876, and has recently become an important product for the manufacture of triphenylmethane dyestuffs.

Tetramethyldiamidobenzophenone is obtained by action of carbon oxychloride or of perchlorformic ether on dimethylaniline.

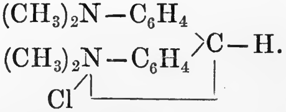
The analogous thioketone already mentioned is obtained in a similar manner from carbon sulphochloride, $CSCl_2$, and dimethylaniline; it may also be obtained by treating the corresponding oxygen ketone with phosphorus sulphide. The two ketones are similar in their reactions [3].

By action of nascent hydrogen, tetramethyldiamidobenzophenone is converted into the corresponding benzhydrol [1]:—

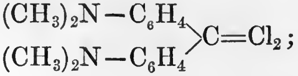


$$\begin{matrix}(CH_3)_2NC_6H_4 \\ (CH_3)_2NC_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}OH \\ H\end{matrix}.$$

This compound combines with acids to form beautiful blue salts, which, like the dyestuffs of the rosaniline series, are decolorised by excess of acid. It is probable that in these coloured salts the compound exists as an anhydride, as is the case with the rosaniline salts. The hydrochloride, for instance, has the constitution:—

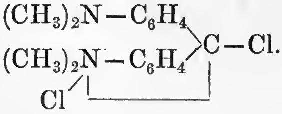


The chloride obtained by treating tetramethyldiamidobenzophenone with a phosphorus chloride is probably not the simple chloride



$$\begin{matrix}(CH_3)_2N-C_6H_4 \\ (CH_3)_2N-C_6H_4\end{matrix}\!\!>C=Cl_2;$$

but, as it possesses a deep blue colour, is constituted according to the formula:—



Auramine [1, 4, 5, 7].

$C_{17}H_{21}N_3$.

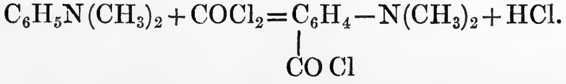
This dyestuff was discovered simultaneously by A. Kern and H. Caro, and is formed by action of ammonia on tetramethyldiamidobenzophenone. It is best prepared by melting this base with ammonium chloride and zinc chloride. The reaction is expressed by the equation :—

$$C_{17}H_{20}N_2O+NH_3=C_{17}H_{21}N_3+H_2O.$$

Another process for the manufacture of auramine consists in allowing ammonia to act on a mixture of tetramethyldiamidodiphenylmethane or tetramethyldiamidobenzhydrol with sulphur at 180°.

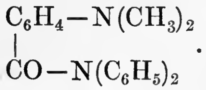
Auramine is also prepared industrially as follows :—

Dimethylamidobenzoic chloride is produced by action of phosgene on dimethylaniline;



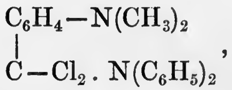
$$C_6H_5N(CH_3)_2+COCl_2=\underset{\displaystyle COCl}{\underset{\vert}{C_6H_4}}-N(CH_3)_2+HCl.$$

This chloride is treated with diphenylamine, whereby dimethylamidobenzodiphenylamine is formed;



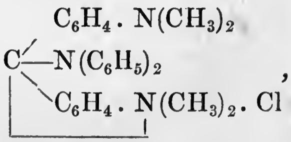
$$\begin{array}{l} C_6H_4-N(CH_3)_2 \\ \vert \\ CO-N(C_6H_5)_2 \end{array}.$$

Practically, the above reactions are combined into one operation. The above condensation-product is treated with a chloride of phosphorus or phosgene, and the resulting chloride,



$$\begin{array}{l} C_6H_4-N(CH_3)_2 \\ \vert \\ C-Cl_2\,.\,N(C_6H_5)_2 \end{array},$$

condensed with dimethylaniline, and the compound produced



$$C\begin{cases} C_6H_4\,.\,N(CH_3)_2 \\ N(C_6H_5)_2 \\ C_6H_4\,.\,N(CH_3)_2\,.\,Cl \end{cases},$$

heated with ammonia yields auramine and diphenylamine.

Auramine comes into commerce as the hydrochloride $C_{17}H_{21}N_3$, HCl. This salt is easily soluble in water, and crystallises from this medium in beautiful golden-yellow leaflets.

It is decomposed by continued boiling with water, especially in presence of free hydrochloric acid, tetramethyldiamidobenzophenone and ammonia being regenerated.

Platinum double salt, $(C_{17}H_{21}H_3,HCl)_2,PtCl_4$, forms an orange-red precipitate.

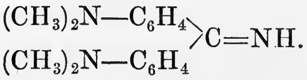
Picrate, $C_{17}H_{21}N_3,C_6H_2(NO_2)_3OH$, forms yellow leaflets sparingly soluble.

Oxalate, $(C_{17}H_{21}N_3)_2C_2H_2O_4$, forms yellow needles sparingly soluble in water.

Leuco-auramine [7], $C_{17}H_{23}N_3$, is formed by reduction of an alcoholic solution of auramine with sodium amalgam. It forms colourless crystals, M.P. 135°, and dissolves in glacial acetic acid with a blue colour (see under).

Phenylauramine and tolylauramine are obtained by action of aniline and toluidine on auramine or on tetramethyldiamidobenzophenone.

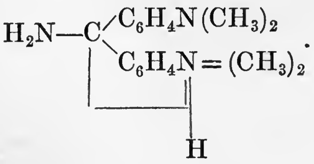
Auramine must be regarded as the imide of tetramethyldiamidobenzophenone, and accordingly has the constitutional formula :—



$$\left.\begin{array}{l}(CH_3)_2N{-}C_6H_4\\(CH_3)_2N{-}C_6H_4\end{array}\right\rangle C{=}NH.$$

The ring constitution accepted for tetramethyldiamidobenzhydrol cannot be present in auramine, as the elements of constitutional water necessary are not present. The yellow colour of auramine also is against the assumption of a ring formula, the benzhydrols being blue.

On the other hand, a ring-formation is probably present in the blue salt formed by leucoauramine and acetic acid, and this Graebe expresses by the formula :—



An objection to this formula is that till now pentatomic nitrogen is only known in combination with an acid radical or hydroxyl. Auramine and its derivatives are the only dyestuffs known which belong to the class of simple ketoneimides. The chromophor, C=NH, unlike that in rosaniline dyestuffs, occurs in an open chain, and in this respect the hydrazides (Tartrazine) are similar, and also have a yellow colour. Auramine is one of the few basic yellow dyestuffs, and owing to its easy fixation on tannin mordants has obtained a considerable importance in cotton-dyeing and printing. It produces a pure yellow shade.

Its substitution-derivatives, such as phenylauramine, have mostly a brown colour, and have not been applied practically.

PHENYLHYDRAZIDES [8].

Phenylhydrazine reacts readily with most compounds which contain the group CO; the oxygen atom being eliminated in the form of water with two hydrogen atoms of the phenylhydrazine, the rest of the latter entering in the place of the oxygen.

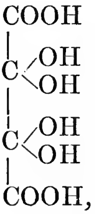
It is probable that the two hydrogen atoms which split off belong to the amido-group, and therefore the hydrazides contain the group $C=N—NHC_6H_5$.

That a close relationship exists between azo-compounds and hydrazides is seen from the fact that certain oxyazo-compounds obtained from diazo-compounds and phenols are identical with the hydrazides of certain quinones. Indeed all coloured hydrazides show a great similarity to the azo-compounds, and probably belong to this class. Both classes of compounds, for example, behave similarly on reduction. The hydrazine group, like the azo-group, is split, yielding two amido-groups, one of which remains in combination with the phenyl group, the other with the carbon atom.

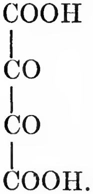
All the hydrazides known at present have a yellow or orange colour, like the simpler azo-compounds.

Tartrazine.

This dyestuff is manufactured by action of phenylhydrazine-sulphonic acid on dioxy-tartaric acid. This acid, which in the hydrated condition has a formula



must be regarded as the hydrate of a diketonic acid:

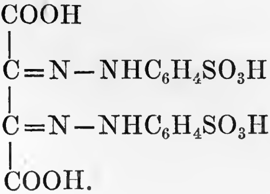


$$\begin{array}{l} COOH \\ | \\ CO \\ | \\ CO \\ | \\ COOH. \end{array}$$

It reacts according to the latter formula with hydrazines, two molecules of which enter into reaction.

The product obtained with two molecules of phenylhydrazine has a beautiful yellow colour; it is too sparingly soluble to be of use in dyeing, but a valuble dyestuff may be obtained by introduction of sulpho-groups.

The commercial product known as Tartrazine is a sulphonic acid prepared by the action of two molecules of phenylhydrazine-sulphonic acid (from sulphanilic acid) on one molecule of sodium dioxytartrate in hydrochloric acid solution. The constitution of tartrazine is probably expressed by the following formula:—



$$\begin{array}{l} COOH \\ | \\ C{=}N{-}NHC_6H_4SO_3H \\ | \\ C{=}N{-}NHC_6H_4SO_3H \\ | \\ COOH. \end{array}$$

The sodium salt of tartrazine forms a fine orange-yellow crystalline powder. It dyes animal fibres from an acid bath, producing a beautiful gold-yellow shade, which is valuable for its stability against light and milling.

The application of higher hydrazines gives rise to dyestuffs of a redder tone.

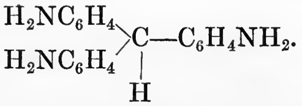
CHAPTER V.

TRIPHENYLMETHANE DYESTUFFS.

Triphenylmethane and its analogues are mother substances of a series of dyestuffs, many of which are of great technical importance.

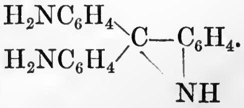
If amido- or hydroxyl-groups are introduced into triphenylmethane, in certain positions, colourless compounds, the leuco-derivatives of dyestuffs, are formed.

For example, if three amido-groups are introduced into the three benzene nuclei, in the para position to the methane-carbon atom, the compound known as paraleucaniline is formed,



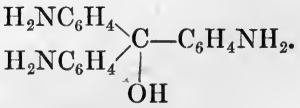
$$\left.\begin{matrix}H_2NC_6H_4\\H_2NC_6H_4\end{matrix}\right\rangle \underset{\displaystyle H}{\underset{|}{C}}-C_6H_4NH_2.$$

On oxidation this compound loses two hydrogen atoms, and a condensation takes place between the nitrogen of an amido-group and the methane-carbon atom, pararosaniline being formed. [See Introduction.]



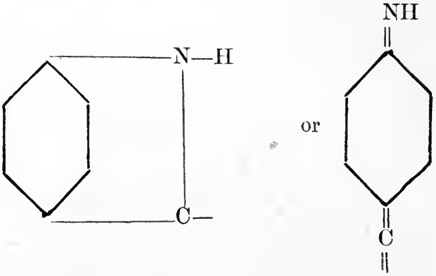
$$\left.\begin{matrix}H_2NC_6H_4\\H_2NC_6H_4\end{matrix}\right\rangle C-\underset{\displaystyle NH}{\underset{|}{C_6H_4}}.$$

Pararosaniline only exists in the form of its salts, and in the free state takes up one molecule of water, triamidotriphenylcarbinol, a colourless compound, being formed,



$$\left.\begin{matrix}H_2NC_6H_4\\H_2NC_6H_4\end{matrix}\right\rangle \underset{\displaystyle OH}{\underset{|}{C}}-C_6H_4NH_2.$$

This transformation into colourless carbinol-derivatives takes place with all basic triphenylmethane dyestuffs, and the carbinols are for this reason regarded as the bases of the dyestuffs, although this assumption is not altogether correct. Really both classes of compounds have totally different constitutions, as in the dyestuffs a closed ring is present, while in the carbinols it is absent. In the triphenylmethane dyestuffs the chromophor $\equiv$C—NH— or $\equiv$C—O— is always present, and generally effects the linkage between several aromatic nuclei. In most cases it occurs, however, in one ring, occupying two para positions. For instance, pararosaniline contains the group:



which shows a certain analogy to quinones.

The imido-group present in the chromophor also serves as salt-forming group, and appears to effect a combination of the dyestuff with the fibre. For instance, animal fibres may be dyed with the colourless carbinol bases, just as with the dyestuffs themselves. Apparently a salt is formed, in which the fibre acts as an acid, and combines with the imido-group.

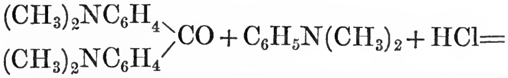
The basic properties of the amido-groups present only become apparent under the influence of strong acids, or of the haloid derivatives of the alcohol radicals. These amido-groups, however, intensify the basicity of the imido-group. The formation of salts with these groups is generally attended by a striking alteration of the dyestuff character.

Basic triphenylmethane dyestuffs mostly form sulphonic acids; these are generally acid dyestuffs, and when observed in the free state or in form of their acid salts have the same colour as the original dyestuffs. Their neutral alkali salts are colourless, and appear to be carbinol compounds.

The conversion of basic carbinols into dyestuffs is generally gradual, and in many cases the formation of colourless salts of the former may be observed. Tetramethyldiamidotriphenylcarbinol (the base of malachite green) gives a colourless solution with dilute acetic acid, the formation of dyestuff only taking place on warming or after long standing.

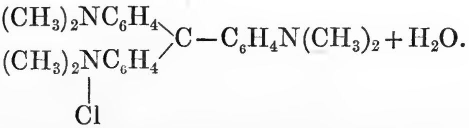
Numerous methods are employed for the production of triphenylmethane dyestuffs.

Substituted benzophenones may be condensed with tertiary bases in presence of a dehydrating agent.



$$\left.\begin{matrix}(CH_3)_2NC_6H_4\\(CH_3)_2NC_6H_4\end{matrix}\right> CO + C_6H_5N(CH_3)_2 + HCl =$$

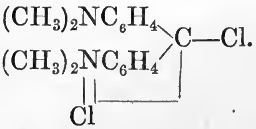
Tetramethyldiamidobenzophenone. Dimethylaniline.



$$\left.\begin{matrix}(CH_3)_2NC_6H_4\\(CH_3)_2NC_6H_4\\ \mid\\ Cl\end{matrix}\right> C - C_6H_4N(CH_3)_2 + H_2O.$$

Hexamethylrosaniline.

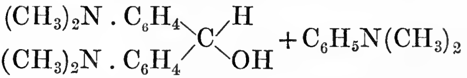
The chloride of tetramethyldiamidobenzophenone reacts in a similar manner. This compound has a blue colour, and probably belongs to the diphenylmethane dyestuffs, which are analogous to the rosanilines. It has the constitution :—



$$\left.\begin{matrix}(CH_3)_2NC_6H_4\\(CH_3)_2NC_6H_4\\ \parallel\\ Cl\end{matrix}\right> C - Cl.$$

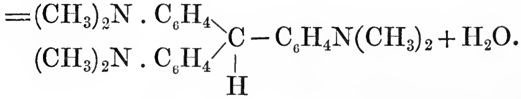
Benzhydrol obtained by reduction of tetramethyldiamidobenzophenone (compare page 94), and which also in form of its salts behaves like a dyestuff, reacts with amines with the greatest ease.

In this reaction the leuco-derivatives of the dyestuffs are obtained.



$$\begin{matrix}(CH_3)_2N\,.\,C_6H_4\\(CH_3)_2N\,.\,C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}H\\OH\end{matrix} + C_6H_5N(CH_3)_2$$

Tetramethyldiamidobenzhydrol. Dimethylaniline.



$$=\begin{matrix}(CH_3)_2N\,.\,C_6H_4\\(CH_3)_2N\,.\,C_6H_4\end{matrix}\!>\!\underset{\underset{H}{|}}{C}-C_6H_4N(CH_3)_2+H_2O.$$

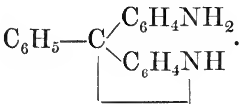
Hexamethylparaleucaniline.

Colouring-matters (rosaniline, methyl violet) of this class are also formed by oxidation of primary, secondary, or tertiary amines, which contain methyl groups in combination with nitrogen or carbon. Further, benzene-derivatives, which contain no methyl groups, yield dyestuffs if treated with compounds which at the same time are capable of withdrawing hydrogen and supplying carbon, such as carbon tetrachloride, oxalic acid, iodoform (rosolic acid, diphenylamine blue). Another method consists in the direct introduction of amido-groups into triphenylmethane. Again, aromatic bases or phenols yield triphenylmethane-derivatives by condensation with toluenes, chlorinated in the side chain, or with aromatic aldehydes. In most of these cases leuco-compounds are obtained, and are converted into dyestuffs by oxidation. The phthaleïns, a peculiar class of triphenylmethane dyestuffs, are prepared by condensation of phthalic anhydride with phenols.

A. ROSANILINE DYESTUFFS.

In the wider sense of the term, this class comprises all the basic dyestuffs obtained from triphenylmethane and its homologues. As has already been remarked, the salts are the real dyestuffs, while the so-called colour-bases are colourless carbinol derivatives. Up to the present, no suitable nomenclature has been applied to the actual dyestuffs, rosaniline for example being generally called triamidotriphenylcarbinol, and this method has been adopted in the present work; although in reality the carbinol bases have little or nothing to do with the dyestuffs, so far as constitution is concerned.

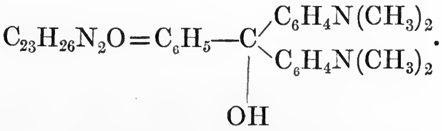
The simpler basic triphenylmethane dyestuffs are derivatives of diamidotriphenylmethane. This compound gives a violet dyestuff on oxidation, which has not been submitted to a close investigation [2]. It is probably a member of the class of compounds in question, and has the constitution :



$$C_6H_5-C\begin{matrix}\diagup C_6H_4NH_2\\ \diagdown C_6H_4NH\end{matrix}.$$

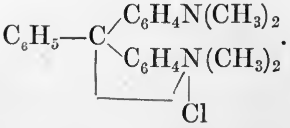
The tetramethyl derivative of the above compound comes next in the series, and is a well-characterized substance.

Tetramethyldiamidotriphenylcarbinol [3, 4, 5].



$$C_{23}H_{26}N_2O=C_6H_5-\underset{\displaystyle OH}{C}\begin{matrix}\diagup C_6H_4N(CH_3)_2\\ \diagdown C_6H_4N(CH_3)_2\end{matrix}.$$

The base, separated from its salts by alkalies, forms a colourless or slightly grey powder. It crystallises from ligroïn in shining colourless leaflets, or in round aggregates of crystals, M.P. 120°. With acids the compound forms intensely green salts, water being split off. As the amido-groups contain no replaceable hydrogen, and as it is scarcely probable that the hydrogen necessary for the formation of water is withdrawn from the methyl group, it may be accepted that the hydrogen atom is displaced from a molecule of the acid, and that the salt formed has a similar constitution to the salts of quaternary ammonium bases. Accordingly the hydrochloride has the constitutional formula [3] :



$$C_6H_5-C\begin{matrix}\diagup C_6H_4N(CH_3)_2\\ \diagdown C_6H_4\underset{\displaystyle Cl}{N}(CH_3)_2\end{matrix}.$$

With a large excess of acid, the pale yellow diacid salt may be obtained. The monoacid salts are characterized by the ease with which they crystallise; they are beautiful green dyestuffs of great tinctorial power [5].

Hydrochloride, $C_{23}H_{24}N_2,HCl$, forms easily soluble green leaflets.

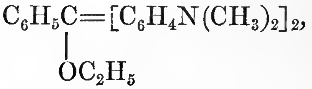
Sulphate, $C_{23}H_{24}N_2,H_2SO_4$, crystallises with one molecule of H_2O in brilliant green needles, or anhydrous in thick green prisms.

Zinc chloride double salt, $(C_{23}H_{24}N_2,Cl)_3 + 2ZnCl_2 + 2H_2O$, forms brilliant green needles or leaflets.

Oxalate, $2C_{23}H_{24}N_2 + 3C_2H_2O_4$, large green prisms, easily soluble in water.

Picrate sparingly soluble, crystallises in golden-yellow needles.

Ethyl ether,



$$C_6H_5\underset{\displaystyle OC_2H_5}{\underset{|}{C}}=[C_6H_4N(CH_3)_2]_2,$$

is obtained by heating the base with alcohol to 110°; it is colourless, and melts at 162°.

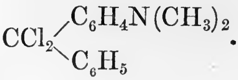
The methyl iodide [5],

$$C_{23}H_{25}(OCH_3)N_2,2CH_3I + H_2O,$$

is formed by heating the base with methyl iodide and methyl alcohol. It forms colourless needles.

Tetramethyldiamidotriphenylcarbinol, or more correctly its anhydride, is formed by oxidation of tetramethyldiamidotriphenylmethane [3], and by condensation of two molecules dimethylaniline with one molecule benzotrichloride in presence of zinc chloride [4]. It may also be obtained from benzoyl chloride and dimethylaniline [3] by action of the air.

The most recent method of preparation is by action of dimethylaniline on the chloride obtained by treating dimethylamidobenzophenone with phosphorus trichloride.



The salts of tetramethyldiamidotriphenylcarbinol come into commerce under numerous names, of which Malachite Green and Benzaldehyde Green are most usual. Malachite green has attained considerable importance; it has almost treble the tinctorial power of the older methyl green, and possesses further the advantages of dyeing wool easily and resisting the action of heat. The oxalate and the zinc-chloride double salt are most frequently met with.

Malachite green was first prepared by E. and O. Fischer [3] by oxidation of tetramethyldiamidotriphenylmethane. Shortly afterwards Doebner obtained it by action of benzotrichloride on dimethylaniline, a process which was patented [4, 6] and used for the manufacture of the dyestuff. At that time Fischer's method of preparation was not practicable, as the necessary benzaldehyde could not be obtained. However, the difficulties encountered in the technical production of the latter were soon overcome, and now the benzotrichloride process, which gives very unsatisfactory results, has been entirely abandoned. At present the manufacture of malachite green is carried out as follows:—

The leuco-base is prepared by heating one molecule of benzaldehyde with two molecules of dimethylaniline in presence of hydrochloric acid. (Zinc chloride was formerly used, but has been found to be unnecessary.) The base is then dissolved in the theoretical quantity of hydrochloric acid and the calculated amount of finely suspended lead peroxide added to the solution, which must be very dilute. The lead is removed as sulphate by adding sodium sulphate, and the dyestuff precipitated by adding zinc chloride and salt.

Nitro-derivatives of Tetramethyldiamidotriphenylcarbinol [3, 8].

The paranitro-compound is obtained by oxidation of nitrotetramethyldiamidotriphenylmethane (from paranitrobenzaldehyde and dimethylaniline) and also by action of paranitrobenzoyl-chloride and atmospheric oxygen on dimethylaniline [3].

The base, $C_{23}H_{25}N_2O(NO_2)$, crystallises in yellow prisms. The salts are green, and are decomposed by water. On partial reduction a violet dyestuff (probably tetramethylpararosaniline) is formed; complete reduction yields tetramethylparaleucaniline.

The meta-compound [2, 8] is formed by oxidation of the nitrotetramethyldiamidotriphenylmethane obtained from metanitrobenzaldehyde and dimethylaniline. It is similar to the former compound, but does not yield a violet dyestuff on reduction.

Dichlortetramethyldiamidotriphenylcarbinol [11].

$C_{23}H_{24}N_2Cl_2O$.

The salts of this compound come into commerce as Victoria Green 3 B or New solid Green 3 B. It is prepared by condensation of dichlorbenzaldehyde with dimethylaniline and subsequent oxidation of the leuco-base formed. Its shade is bluer than that of malachite green.

Tetraethyldiamidotriphenylcarbinol [7].

$C_{27}H_{32}N_2O$.

The salts of this base come into commerce under the names Brilliant Green, New Victoria Green, Ethyl Green, and Solid Green. The sulphate, $C_{27}H_{32}N_2,H_2SO_4$, is most commonly met with. It forms brilliant, gold shimmering needles. The zinc-chloride double salt forms brilliant green needles. In dyeing brilliant green produces yellower shades than malachite green.

Sulphonic Acids [9, 10].

These bodies are in considerable demand, especially for wool-dyeing, and numerous products are met with in commerce. They are generally prepared by sulphonation of the leuco-bases, and subsequent oxidation; as the bases themselves do not give good results on direct sulphonation. The sulpho-group enters especially easily into benzylated bases; and probably enters the benzene ring of the benzyl group.

Helvetia Green.

$C_{23}H_{25}N_2O_4SNa$.

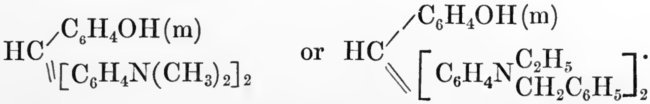
This dyestuff, which is obtained by sulphonation of leuco-malachite green, and subsequent oxidation, is the oldest of its class; but is not much used at present, as its acid properties are only slightly developed.

Light Green S.

$C_{37}H_{35}N_2O_{10}S_3Na.$

This dyestuff is known also as Acid Green, Light Green S F, and Guinea-Green B, and is the most important of this class. The leuco-base used for its production is diethyldibenzyldiamidotriphenylmethane, obtained by condensation of ethylbenzylaniline and benzaldehyde. The resulting body is sulphonated and oxidised. Light Green S F dyes wool and silk from an acid bath (Friedlander, B.B. 1889, p. 588).

Certain blue dyestuffs which belong to this class have recently been introduced into the market. They are prepared by condensation of dimethylaniline, diethylaniline, and ethylbenzylaniline with metaoxy- or meta-amidobenzaldehyde. The resulting leuco-bases have the formulæ:—

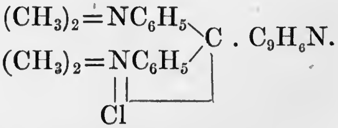


$$HC\begin{cases} C_6H_4OH(m) \\ [C_6H_4N(CH_3)_2]_2 \end{cases} \quad \text{or} \quad HC\begin{cases} C_6H_4OH(m) \\ \left[C_6H_4N\begin{matrix}C_2H_5\\CH_2C_6H_5\end{matrix}\right]_2 \end{cases}.$$

The commercial dyestuffs known as *Patent Blue N* and Superfine are lime-salts of the sulphonic acids, obtained by sulphonation and subsequent oxidation of the above leuco-bases. The shades produced are similar to those of indigo extract, and have the advantage of greater fastness and brilliancy (D. R. P. 46384, 48523; Chemikerz. 1889, p. 1702).

A further dyestuff derivative of diamidotriphenylmethane is Quinoline Green [1], obtained by action of tetramethyldiamidobenzophenone, its chloride, or its hydrol on quinoline. In the last case a leuco-compound is formed.

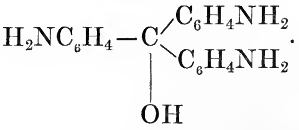
The dyestuff is probably constituted according to the formula:—



$$\begin{matrix}(CH_3)_2{=}NC_6H_5 \\ (CH_3)_2{=}NC_6H_5 \\ | \\ Cl\end{matrix} \!>\! C \,.\, C_9H_6N.$$

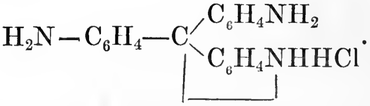
Acid Violet N is a dyestuff of similar properties, and probably of similar constitution to the above.

Triamidotriphenylcarbinol, Pararosaniline.



$$H_2NC_6H_4-\underset{\displaystyle OH}{C}\begin{matrix}C_6H_4NH_2\\C_6H_4NH_2\end{matrix}.$$

The anhydride occurs only in the coloured salts; for example, in the hydrochloride :—



$$H_2N-C_6H_4-C\begin{matrix}C_6H_4NH_2\\C_6H_4NHHCl\end{matrix}.$$

The amido-groups of pararosaniline are in the para position to the methane-carbon atom. It is formed by heating two molecules of aniline and one molecule of paratoluidine [11] with arsenic acid, mercuric chloride, or other oxidizing agents; by partial reduction of trinitrotriphenylcarbinol with zinc powder and acetic acid [12]; by oxidation of triamidotriphenylmethane (paraleucaniline) [12]; by heating aurine with ammonia to 120° [12]; and by heating pure aniline with carbon tetrachloride, ethylene chloride, or iodoform. It may also be obtained by action of paranitrobenzaldehyde [14], paranitrobenzyl- and benzoyl chloride [15], or paranitrobenzyl-alcohol on aniline.

The base forms colourless leaflets sparingly soluble in cold, more easily in hot water. It combines with one molecule of acid to form salts of an intense red colour. With an excess of acid, yellow triacid salts are formed, which are decomposed by water.

On reduction, pararosaniline yields paraleucaniline (triamidotriphenylmethane).

By heating with hydriodic acid in a sealed tube it splits up into aniline and paratoluidine. Pararosaniline was discovered by Rosenstiehl [16], and its constitution determined by E. and O. Fischer [12]. The above constitutional formula is deduced from the following facts :—

On treating with nitrous acid, pararosaniline gives a hexazo-compound, in which all three nitrogen groups are present as diazo-groups (probably carbinol compound). On boiling with alcohol this diazo-compound yields triphenylmethane, $C_{19}H_{16}$.

On partial reduction trinitrotriphenylcarbinol yields pararosaniline [12]; paraleucaniline being formed on further reduction.

By action of paranitrobenzaldehyde on aniline in presence of zinc chloride, nitrodiamidodiphenylmethane is formed; yielding paraleucaniline on reduction [12].

Pararosaniline is present in most commercial rosanilines. Its salts are similar to those of the latter, but are in general somewhat more easily soluble in water.

The synthesis of pararosaniline (from paranitrobenzaldehyde, &c.) [14, 15, 17, 18] has until now not been carried out on a large scale, but it may be expected that in course of time the technical difficulties which stand in the way of these processes will be overcome. Recently pararosaniline has been manufactured by a synthetic process based on the following lines. Anhydroformaldehydeaniline, obtained by action of formaldehyde on aniline, is heated with aniline and aniline hydrochloride, whereby diamidodiphenylmethane is formed. This latter compound, on heating with aniline, aniline hydrochloride, and an oxidising agent yields pararosaniline.

Methyl Violet [19].

The commercial products known under this name are prepared by oxidation of dimethylaniline sometimes containing monomethylaniline. The dimethylaniline is mixed with sulphate or chloride of copper, acetic acid, potassium chlorate, and a large quantity of common salt. A more recent process consists in using phenol in place of acetic acid—the chlorate being generally dispensed with. During the actual process the cupric chloride becomes reduced to cuprous chloride, which oxidises again at the expense of the chlorate or by the atmospheric oxygen, thus acting as oxygen-carrier. Cuprous chloride is capable of forming an almost insoluble double chloride with methyl violet, this property being absent in cupric chloride. Formerly the double compound was decomposed by sulphuretted hydrogen, the soluble violet being separated from copper sulphide by filtration. At present the same end is attained by addition of ferric chloride, which oxidises the cuprous salt to cupric chloride, which remains in the mother-liquor after the violet has been salted out.

The following will give an idea how the phenol process is carried out on a large scale. The operation takes place in a drum, which is jacketed, and connected with steam- and cold-water supplies. Finely powdered salt and copper sulphate are stirred with phenol and a little water to a homogeneous mixture. Dimethylaniline is then added, and the whole heated to 55°, with continual stirring, care being taken that the temperature does not rise above 60°. After a few hours the cover is removed, to allow the air to act, the temperature being maintained at 55°. The process is ended in about 8 hours, and the melt is cooled by passing cold water into the casing of the drum. The melt is dissolved in water, and the base of the dyestuff precipitated, along with copper oxide, by addition of milk of lime, and the precipitate washed to remove soluble salts. It is then suspended in water, and treated with sulphuretted hydrogen, whereby copper sulphide is formed, and being insoluble in hydrochloric acid, the violet may be obtained in solution by heating the precipitate with this acid. Finally, the dyestuff is precipitated from the acid solution by salt, and purified by repeated solution and reprecipitation by salt.

An older process, now abandoned, possesses interest from a theoretical standpoint. In this case no chlorine compound was used, the mixture consisting of dimethylaniline, copper sulphate, acetic acid, and sand. The violet is precipitated from the solution of the melt as sulphate by sodium sulphate. The absence of chlorine prevents the formation of the insoluble double chloride, and the reduced copper compound is got rid of as insoluble suboxide.

The *rôle* played by the phenol in the modern process of manufacture has not been explained, but it is certain that its presence considerably increases the yield of the dyestuff.

Methyl violet is produced by action of other oxidising agents on dimethylaniline, such as iodine and chloranil. According to Brunner and Brandenburg bromine acts on dimethylaniline, forming a brominated methyl violet [21]. On the other hand, the dyestuff is not produced by oxidation of dimethylaniline in acid solution, with lead peroxide, manganese dioxide, or chromic acid.

As yet, the chemistry of the methyl-violet process is little understood. According to E. and O. Fischer [12], a methyl group is partly oxidised, and the formic acid produced thereby serves to link the benzene nuclei together, and to supply the necessary methane-carbon atom. As, however, the formation of violet is difficult to follow, it is not easy to give an explanation of the reactions involved in its production.

In fact O. Fischer and Koerner have obtained hexamethylparaleucaniline quantitatively by action of the methyl ether of orthoformic acid on dimethylaniline [22]. The violet from dimethylaniline and chloranil is apparently identical with the ordinary one obtained by the copper process [23].

Methyl violet forms amorphous masses with a green lustre. It is easily soluble in water, and dyes wool and silk violet from a neutral bath. On addition of a mineral acid, the solution of the violet becomes first blue, then green, and finally dirty yellow.

The commercial product is a mixture, consisting chiefly of pentamethyl- and tetramethyl-pararosaniline with some hexamethylpararosaniline.

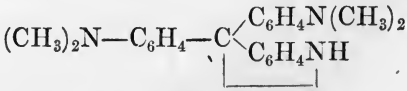
If prepared from dimethylaniline containing monomethylaniline, the violet also contains lower methylated rosanilines.

As the blue shade of the violet increases with the number of methyl groups, the bluest brands are richest in hexamethyl compounds. Blue shades of violet are also obtained by action of benzyl chloride on the violet-base. According to Fischer the benzyl group does not attack hexamethylpararosaniline, only the lower methylated products yielding benzylated violets [25].

The dyestuffs known as *acid-violets* are mostly sulphonic acids of benzylated methyl violets.

Methyl violet is difficult to convert into sulphonic acid by fuming sulphuric acid; a better result is obtained by sulphonation, and subsequent oxidation of the leuco-base. Benzylated violets, however; are much easier to sulphonate, especially in form of their leuco-bases, the sulpho-group probably entering the benzene nucleus of the benzyl group. Other acid-violets are obtained by methylation and benzylation of acid magenta.

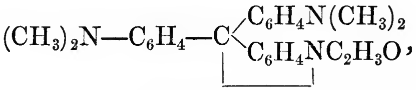
Tetramethylpararosaniline [24].



$$(CH_3)_2N{-}C_6H_4{-}C\begin{matrix}\diagup C_6H_4N(CH_3)_2\\ \diagdown C_6H_4NH\end{matrix}$$

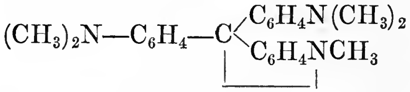
This violet dyestuff was prepared by Fischer by oxidation of tetramethyltriamidotriphenylmethane; it is also obtained by partial reduction of paranitro-malachite green.

Acetyltetramethylpararosaniline [23],



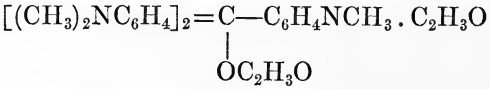
is formed by oxidation of acetyltetramethylparaleucaniline. It is a green dyestuff, and on treating with hydrochloric acid yields tetramethylpararosaniline.

Pentamethylpararosaniline [25].



The pure base is obtained by saponification of its diacetyl derivative with hydrochloric acid. The hydrochloride is a constituent of commercial methyl violet.

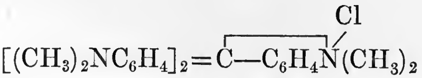
Diacetylpentamethylpararosaniline [25].



$$[(CH_3)_2NC_6H_4]_2{=}\underset{\displaystyle OC_2H_3O}{\underset{|}{C}}{-}C_6H_4NCH_3 \,.\, C_2H_3O$$

May be obtained by treating the crude base of methyl violet with acetic anhydride. It is a colourless base, and gives a green salt with acetic acid. This fact is not easily understood unless under the assumption that one acetyl group splits off, and the oxygen atom of the carbinol group is eliminated.

Hexamethylpararosaniline [23, 25, 26].



This dyestuff is known in commerce as Crystal Violet, and also occurs in Methyl Violet. It is obtained by action of dimethylaniline on tetramethyldiamidobenzophenone:

$$(CH_3)_2NC_6H_4{-}CO{-}C_6H_4N(CH_3)_2$$

in presence of a dehydrating agent, according to the equation

$$C_{17}H_{20}N_2O + C_8H_{11}N,HCl = C_{25}H_{30}N_3Cl + H_2O.$$

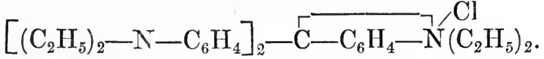
This is effected on a large scale in one operation, phosgene ($COCl_2$) being allowed to act on dimethylaniline in presence of zinc chloride, and further is formed by action of perchlormethylformiate on dimethylaniline in presence of aluminium chloride or zinc chloride. It is also produced by heating its methyl chloride or methyl iodide compound (methyl green) to 110°–120°.

The *hydrochloride* and *zinc double salt* form lustrous green crystals.

The *hydriodide* and *picrate* are sparingly soluble.

On reduction it yields hexamethylleucaniline, which forms leaflets, M.P. 173°.

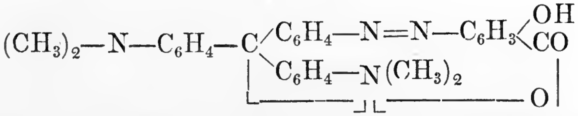
Hexaethylpararosaniline.



$$\left[(C_2H_5)_2{-}N{-}C_6H_4\right]_2{-}C{-}C_6H_4{-}\overset{/Cl}{N}(C_2H_5)_2.$$

This dyestuff comes into commerce as Ethyl Purple, and is prepared by the action of phosgene on diethylaniline. It dyes bluer shades than Crystal Violet.

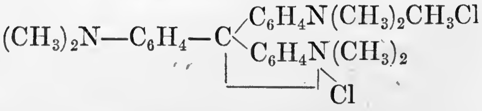
Azo-Green.



$$(CH_3)_2{-}N{-}C_6H_4{-}C\begin{array}{l} \diagup C_6H_4{-}N{=}N{-}C_6H_3\begin{array}{l}\diagup OH\\ \diagdown CO\end{array}\\ \diagdown C_6H_4{-}N(CH_3)_2\\ \qquad\qquad\qquad\qquad O\end{array}$$

Although containing an azo-group, the tinctorial properties of this dyestuff are due to its derivation from triphenyl-carbinol. It is obtained by combining the diazo-compound from metamidotetramethyldiamido-triphenylmethane with salicylic acid. It dyes chromed wool a bright greenish-yellow shade. The corresponding paramido-compound gives a blue dyestuff.

Methyl Green [19, 25].



$$(CH_3)_2N{-}C_6H_4{-}C\begin{array}{l}\diagup C_6H_4N(CH_3)_2CH_3Cl\\ \diagdown C_6H_4N(CH_3)_2\\ \qquad\qquad\quad \diagdown Cl\end{array}$$

(Chlormethylate of Hexamethylpararosaniline Chloride.)

This chloride or the corresponding iodide is formed by the action of methyl chloride or iodide on commercial methyl violet. The tetra- and penta-methylpararosanilines are converted into hexamethylrosaniline; the latter adding on one molecule of methyl chloride or iodide.

On a large scale methyl chloride is used. A slow stream of the gas is passed through an alcoholic solution of methyl violet heated to 40°, and kept neutral by addition of soda. Autoclaves are unnecessary, as methyl chloride is sufficiently soluble in alcohol and no pressure is produced.

The alcohol is then distilled off, and the residue dissolved in water, and unaltered violet precipitated by addition of soda or chalk and common salt.

The pure zinc double salt of methyl green is then precipitated by adding zinc chloride; the precipitate being sometimes washed with alcohol to remove any violet present. In commerce this zinc double salt is generally met with in the form of brilliant green leaflets.

The *iodide,* $C_{26}H_{33}N_3I_2$, forms green needles easily soluble in water [18].

The *picrate,* $C_{26}H_{33}N_3[(C_6H_3)(NO_2)_3OH]_2$, is insoluble in water, sparingly soluble in alcohol.

The base, $C_{26}H_{35}N_3O_2$, is obtained by treating the chlorine or iodine compound with silver oxide. It is colourless, and its alcoholic solution remains colourless on acidifying, the formation of a green salt only taking place on warming. The salts of methyl green decompose at 110° to 120°, methyl chloride or iodide splitting off, and leaving a violet residue of hexamethylrosaniline chloride.

An analogous green is the brom-ethylate obtained by the action of ethyl bromide on methyl violet. The composition of the commercial zinc double salt (ethyl green) is probably

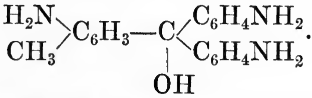
$$C_{25}H_{30}N_3ClC_2H_5BrZnCl_2.$$

An advantage of this ethyl green is that its shade is yellower than that of methyl green. Methyl and ethyl greens dye silk directly, and cotton prepared with tannic acid. Wool cannot be dyed directly, and is either previously mordanted with sulphur by a bath of thiosulphate of soda, or dyed in a bath of methyl green made alkaline with ammonia. Fibres dyed with these greens become violet on heating, and this reaction serves for their identification. At present methyl and ethyl green are scarcely ever used, having been replaced by the cheaper and stronger benzaldehyde greens.

The green colour of a compound appears to require the presence of an ammonium group, and an amido-group not in combination with an acid. Benzaldehyde green, for example, fulfils these conditions. In methyl violet, an ammonium group and two methylated amido-groups are present, and as long as the latter are not in combination with an acid the compound is violet. When, however, one of them is saturated by an acid, the colour changes to green, but the green salts are unstable, and are decomposed by water. Stable green dyestuffs are formed, if the acid is replaced by methyl chloride, the same effect being produced by the introduction of an ethyl group. It appears, therefore, that the neutralisation of the basic properties of the third nitrogenous group has the same effect as its entire removal would have.

Triamidodiphenyltolylcarbinol [12, 28].

(ROSANILINE, MAGENTA, FUCHSINE.)



$$\begin{matrix}H_2N\\CH_3\end{matrix}\!\!>C_6H_3-\underset{\displaystyle OH}{\underset{|}{C}}\!<\!\!\begin{matrix}C_6H_4NH_2\\C_6H_4NH_2\end{matrix}.$$

Rosaniline, a homologue of pararosaniline, is formed by oxidation of equal molecules of orthotoluidine, paratoluidine, and aniline. As oxidising agents, stannic chloride, mercuric chloride or nitrate, arsenic acid, or nitrobenzene may be used. Mercuric nitrate, arsenic acid, and nitrobenzene have been applied on a large scale; but at present the two latter are the only oxidants used technically. The arsenic acid process is carried out in a boiler fitted with a stirrer, and connected with a cooling-worm. Aniline of approximately the above composition (aniline for red) and syrupy arsenic acid (containing about 70 per cent. arsenic anhydride) are introduced, and the mixture is heated to 170°–180°. Part of the aniline oil used distils over during the operation, which generally lasts 8 to 10 hours. As soon as the melt has attained a certain condition, it is allowed to flow out, and after cooling is broken up. It is then boiled with water in a closed vessel under pressure, the arsenic and arsenious acids being at the same time partly neutralised by addition of lime. After filtering, the rosaniline hydrochloride is separated from the filtrate by addition of salt. It is purified by recrystallisation. Magenta prepared by this process generally contains arsenic. In the nitrobenzene process, aniline for red is heated with hydrochloric acid, nitrobenzene, and iron, the process being carried out in much the same manner as above. The iron serves to start the process, by forming ferrous chloride, which is oxidised to ferric chloride by the nitrobenzene, which latter salt in turn effects the oxidation of the aniline.

Nitrobenzene appears to take no part in the formation of rosaniline, and simply acts as oxidant, being converted to dyestuffs of the induline class. When nitrobenzene is replaced by chlornitrobenzene, rosaniline is produced, and not, as might be expected, a chloro-derivative. Dyestuffs of the rosaniline series are formed by oxidation of numerous bases in presence of aniline and paratoluidine. Rosenstiehl and Gerber divide the homologues of aniline into three classes, according to their behaviour on oxidation with arsenic acid.

The first class includes bases which do not yield a magenta on oxidation alone, but do if oxidised in presence of aniline. These bodies are paratoluidine, asymmetric α-metaxylidine, cumidine, and amidotetra- and amidopenta-methylbenzene.

The second class comprises those bases which yield no magenta on oxidation with arsenic acid, but do so if oxidised in presence of a base of the first class. These bases are aniline, orthotoluidine, and γ-metaxylidine. The bases of the third class, metatoluidine and β-metaxylidine, do not yield magenta under any conditions.

In the first class, one methyl group is in the para position to the amido-group, while in the second and third classes the para position is free. In the second class the groups are in the ortho position, and in the third class in the meta position to the amido-group. E. and O. Fischer's experiments have proved that, in the simplest rosaniline, the three amido-groups are in the para position to the fundamental carbon atom. The complete analogy of the homologuous rosanilines with the first having been proved, it can be readily understood why the members of the first group, when oxidised by themselves or with each other, do not yield rosaniline, but do so in presence of aniline.

In the bases of the second class, the para position is free, and one or two ortho positions are occupied. It is clear that these bases cannot yield rosanilines unless they are oxidised with a base of the first group. Neither can the bases of the first class produce magentas, but no reasons yet given can explain why they should not be able to produce rosanilines, when oxidised with other members of the first class. The experiments of Monnet, Reverdin and Noelting and O. Fischer and Koch have, however, confirmed this experiment. Noelting has recently extended our knowledge of the behaviour of the homologues of aniline in this direction. He examined bases in which both the meta and ortho positions are occupied, and found that such bases do not yield magenta under any conditions, and therefore belong to the third class. Metamethylated paratoluidines yield magenta on oxidation in presence of aniline, whether the ortho position be occupied or not.

The investigations on this subject are best summarised as follows :—All paramethylated anilines, paratoluidine, α-metaxylidine, α-orthoxylidine, mesidine, pseudocumidine, isocumidine, the cumidine of Noelting and Forel, isoduridine, phrenidine, and pentamethylamidobenzene yield magentas on oxidation with two molecules of aniline, orthotoluidine, or v-metaxylidine, but do not if oxidised with para free but methylated anilines as metatoluidine, paraxylidine, v-orthoxylidine, s-metaxylidine, the cumidines of Edler and Mayer, and crystallised duridine.

The commercial dyestuff is the hydrochloride of rosaniline; the acetate, however, is also sometimes met with. The free base is also prepared for the manufacture of aniline blue.

Rosaniline-base [28].

$C_{20}H_{21}N_3O$.

Free rosaniline crystallises in colourless leaflets, which become red on exposure to the air. It is sparingly soluble in cold water, somewhat more easily in hot water, and still more easily in alcohol. It is sparingly soluble in ether.

Rosaniline is capable of expelling ammonia from a boiling solution of ammonium chloride, while in the cold rosaniline is precipitated from a solution of its salts by ammonia.

The base is obtained technically by boiling the hydrochloride (magenta) with the calculated amount of lime or caustic soda, and a large quantity of water. The filtered solution deposits the base on cooling, in form of colourless leaflets which become brownish on exposure to air.

By heating with water to 235°, rosaniline decomposes, yielding phenol, ammonia, a base $C_{20}H_{20}N_2O_2$, M.P. 176°, and an acid $C_{20}H_{19}NO_3$ [25]. At 270° ammonia, phenol, and dioxybenzophenone $HO—C_6H_4COC_6H_4—HO$ are formed [26].

The salts [24] of rosaniline, like those of pararosaniline, are formed with a simultaneous elimination of water. The monoacid salts have an intense red colour; the diacid salts are yellowish-brown [24]. The salts are converted into a tertiary diazo-compound by the action of nitrous acid [12].

Hydrochloride, $C_{20}H_{19}N_3,HCl+4H_2O$, occurs as large octohedra or rhombic tables, which have a green metallic reflex. It is with difficulty soluble in cold water, easily in hot water and alcohol.

Acid salt, $C_{20}H_{19}N_3,(HCl)_3$, forms brownish-yellow needles, easily soluble in water, and decomposed by an excess, or at 100°.

Platinum salt, $(C_{20}H_{20}N_3Cl_2)(PtCl_4)_3$.

Hydrobromide, $C_{20}H_{19}N_3,HBr$, is sparingly soluble.

Sulphate, $(C_{20}H_{19}N_3)_2H_2SO_4$, forms brilliant green crystals, sparingly soluble in water.

Acetate, $C_{20}H_{19}N_3,C_2H_4O_2$, forms large green crystals, easily soluble in water.

Picrate, $C_{20}H_{19}N_3,C_6H_2(NO_2)_3OH$, forms needles, sparingly soluble in water.

The *tannate* forms a red precipitate insoluble in water.

Rosaniline and pararosaniline form colourless unstable compounds with sulphurous acid and bisulphites. These compounds react with aldehydes, forming peculiar dyestuffs (Detection of Aldehydes [29]).

Rosanilinesulphonic Acid [30].

(MAGENTA S, ACID MAGENTA.)

By the action of strong fuming sulphuric acid on magenta at 120°, a sulphonic acid, probably the disulphonic acid, is formed. This acid has an intense red colour, and the solutions of its salts are not turned yellow by acids like those of magenta. The neutral salts, with the alkalies and metallic oxides, are colourless, the acid salts being red. Both are easily soluble in water, and difficult to crystallise. From the colour of the acid it is probable that the sulpho- and amido-groups are combined to form a salt, while the colourless salts contain the carbinol group.

Rosanilinesulphonic acid dyes wool and silk from an acid bath, and finds extensive application in dyeing.

Tetrabromrosaniline [31]

is formed by the action of bromine on rosaniline. It is a colourless base, forming violet salts.

At present the researches of E. and O. Fischer and others have led to some confusion as to the exact composition of the methylrosanilines examined by Hofmann. If methyl green is heptamethylpararosaniline, iodine green is not penta- but heptamethylrosaniline, and the violet formed on heating is hexamethylrosaniline. The analytical results obtained by Hofmann scarcely admit of this interpretation. In the present work these bodies are described under the older formulæ, with the hope that further researches may elucidate the matter.

Trimethylrosaniline [28],

$C_{20}H_{18}(CH_3)_3N_3O$.

The hydriodide, $C_{23}H_{26}N_3I$, is formed by heating rosaniline with methyl iodide and methyl alcohol. It is a violet dyestuff sparingly soluble in water.

Tetramethylrosaniline [28],

$C_{20}H_{17}(CH_3)_4N_3O$,

is obtained by heating iodine green to 120°. The iodide, $C_{24}H_{28}N_3I$, forms long bluish-violet needles.

Pentamethylrosaniline [32]. (IODINE GREEN.)

The *iodide*, $C_{20}H_{17}(CH_3)_4N_3I,CH_3I+H_2O$, is prepared by heating rosaniline with methyl iodide and methyl alcohol to 100°. It is freed from any violet dyestuff present in the same manner as methyl green.

The iodide forms metallic prisms easily soluble in water. When heated to 100°–120° methyl iodide splits off, leaving tetramethylpararosaniline.

The *zinc double salt*, $C_{25}H_{31}N_3Cl_2,ZnCl_2$, forms large green crystals. Its solutions are turned yellowish-green by acids.

The *picrate*, $C_{25}H_{29}N_3C_6H_3(NO_2)_3O$, forms prisms with a coppery reflex, which are insoluble in water and sparingly soluble in alcohol.

Before the introduction of methyl green, iodine green was extensively used in dyeing.

Hexamethylrosaniline [32].

The iodide, $C_{20}H_{14}(CH_3)_6N_3I$, is formed along with octomethylleucaniline by heating iodine green with methyl alcohol in a sealed tube to 100°. It forms brownish-green needles, insoluble in water and sparingly soluble in alcohol. It is a violet dyestuff.

Triethylrosaniline [28]. (HOFMANN'S VIOLET.)

$C_{20}H_{18}(C_2H_5)_3N_3O$.

The iodide, $C_{26}H_{35}N_3I_2$, is obtained by heating rosaniline with ethyl iodide and alcohol. It forms brilliant green needles, soluble in alcohol and sparingly so in water. It was formerly manufactured on a large scale.

Tetraethylrosaniline [28].

The iodide has the formula $C_{20}H_{16}(C_2H_5)_4N_3I$.

Tribenzylrosaniline-methyliodide,

$C_{20}H_{16}(C_7H_7)_3N_3CH_3I$,

is prepared by treating rosaniline with benzyl chloride, methyl iodide, and methyl alcohol. It forms green needles insoluble in water [33].

Acetylrosaniline [34],

$C_{20}H_{18}(C_2H_3O)N_3$,

is formed when rosaniline hydrochloride is heated with acetamide. It dissolves in alcohol with a red colour, and forms violet salts.

Triacetylrosaniline [35],

$C_{20}H_{16}N_3(C_2H_3O)_3$,

and *Tribenzoylrosaniline* [35],

$C_{20}H_{16}N_3(C_7H_5O)_3$,

are obtained by the action of acetyl chloride and benzoyl chloride respectively on rosaniline. They are colourless bases forming orange salts.

Compounds of rosaniline with aldehydes have been described by H. Schiff (Ann. cxl. p. 101).

The yield of magenta obtained on a large scale by either of the processes already described is very poor, and seldom exceeds 33 per cent. of the weight of the bases employed. A large quantity of bye-products is formed, and little is known as to their nature. A constant product of the arsenic acid process is a small quantity of chrysaniline. Besides this, various violet and bluish-black products are formed, some of which are soluble in water, some in alcohol, and others are totally insoluble. Some of these dyestuffs dissolve and remain in the mother-liquor of the magenta, but by far the greater part occur in the insoluble residue. From the latter Girard, Delaire, and Chappotot [36] have isolated three bases, viz.:—mauvaniline, $C_{19}H_{17}N_3$, violaniline, $C_{18}H_{15}N_3$, and chrysotoluidine, $C_{21}H_{21}N_3$. However, sufficient analytical data are not forthcoming to support these formulæ, and it is doubtful whether the products examined were really chemical individuals. Possibly violaniline is identical with the simplest induline, and chrysotoluidine with chrysaniline, especially as dyes of the induline series occur in the the magenta-residues (see Indulines).

Aniline Blue [37].

Aniline reacts with rosaniline at 180° in presence of certain organic acids, ammonia being evolved, and phenyl-groups entering into the rosaniline molecule. According to the number of phenyl-groups introduced, the shade of the compound produced varies from violet to pure blue. It is not possible to introduce more than three phenyl-groups into the rosaniline molecule. Acetic acid, benzoic acid, and stearic acid have been used technically, but at present benzoic acid alone is used, as by its aid the best results are obtained both as regards yield and shade of blue (greenish). The action of organic acids in the blue process has not yet been explained. Rosaniline heated with aniline without an organic acid does not yield a blue; a blue is, however, formed from rosaniline and paratoluidine. Only a minute quantity of benzoic acid is required to effect the formation of blue, but in presence of a larger quantity the results are better, and the process is more rapid. At the end of the reaction, benzoic acid remains in the melt unaltered, and may be almost entirely recovered by extraction with alkali.

The amount of aniline used in the manufacture of blue is of great importance. In presence of a large excess of aniline the phenylation is more complete and rapid than when a small quantity is used. For production of pure triphenylrosaniline (green shade of blue) a large excess of aniline is used (ten times the theoretical amount) along with a correspondingly large amount of benzoic acid. The higher homologues of aniline, especially orthotoluidine, give redder shades of blue, and it is therefore necessary to use an aniline as pure as possible. It is required that commercial "aniline for blue" should distil within one degree, and is thus almost chemically pure aniline. For the manufacture of a reddish shade of blue, smaller quantities of benzoic acid and aniline are used, and a less pure aniline-oil is applicable. On a large scale aniline blue is prepared approximately as follows :—

The mixture of the requisite quantities of rosaniline base, benzoic acid, and aniline is brought into a vessel fitted with stirrer and distilling arrangement, and heated to the boiling-point of the aniline. As the blue is contained in the melt in form of the colourless base the progress of the reaction cannot be ascertained by simple inspection. For this purpose portions are removed from time to time, and dissolved in alcohol and acetic acid, the operation being interrupted as soon as the test shows that the desired shade has been reached. According to the shade of blue required, the process may last two to four hours, but if the heating is protracted, some of the blue is liable to be destroyed.

On partly saturating the melt with concentrated hydrochloric acid, the hydrochloride of triphenylrosaniline separates out almost in a state of chemical purity, while impurities remain dissolved in the concentrated solution of aniline in aniline hydrochloride. This latter is separated and saturated with dilute acid, and the precipitate is worked up for inferior blue. This method of purification has completely replaced the older process with alcohol.

The salts of the lower phenylated rosanilines dissolve easily in alcohol, while those of triphenylrosaniline are very sparingly soluble. A very large number of marks of blue come into commerce, the shades being influenced firstly by the degree of phenylation, and secondly by the number of sulpho-groups introduced for the production of soluble blue. Other brands, again, are obtained from the lower quality of blue already mentioned.

i. *Monophenylrosaniline.*

$C_{20}H_{20}N_3(C_6H_5)O.$

The hydrochloride forms brilliant bronzy crystals, soluble in alcohol with a reddish-violet colour [39].

ii. *Diphenylrosaniline.*

$C_{20}H_{19}N_3(C_6H_5)_2O$.

This base forms bluish-violet salts [28, 38].

iii. *Triphenylrosaniline.* (ANILINE BLUE.)

$C_{20}H_{18}N_3(C_6H_5)_3O$.

The free base is colourless and easily soluble in alcohol [28, 37, 38].

The *hydrochloride,* $C_{20}H_{17}N_3(C_6H_5)_3HCl$, is the technical product obtained first in the fractional precipitation of the blue melt with hydrochloric acid. In this state it forms brilliant green crystals, insoluble in water and sparingly soluble in hot alcohol. Aniline dissolves it somewhat more easily. The alcoholic solution has a pure blue colour. Some of this product is used as "spirit-blue," but by far the greater quantity is used for the manufacture of soluble blues. Triphenylrosaniline salts dissolve in sulphuric acid with a brown colour.

The *sulphate* ($C_{20}H_{16}N_3(C_6H_5)_3H_2SO_4$) is almost insoluble in alcohol.

iv. *Sulphonic Acids of Triphenylrosaniline.*

The difficulties encountered in the sulphonation of rosaniline are altogether absent in that of the phenylated rosanilines. A monosulphonic acid is formed by the action of concentrated sulphuric acid at a comparatively low temperature, while by a more energetic sulphonation two, three, and even four sulpho-groups may be introduced into the molecule.

From the foregoing it appears probable that the sulpho-groups enter the phenyl groups and not the rosaniline nucleus.

The sulphonic acids are all amorphous, and possess a blue colour. The salts of the acids are, on the contrary, colourless and probably carbinol derivatives.

Monosulphonic Acid.

$C_{38}H_{30}N_3SO_3H$.

This is the first product of the action of sulphuric acid on aniline blue. The free acid is obtained as a blue amorphous precipitate, which is insoluble in water. The salts are colourless or nearly so, are easily soluble in water, and cannot be crystallised. The sodium salt forms the "alkali blue" of commerce.

This salt, unlike those of other sulphonic acids, may be fixed on wool and silk from a slightly alkaline bath. It is probable that the basic groups of rosaniline effect this fixation. The shade obtained is not strong, but on development with dilute acid, whereby the free sulphonic acid is liberated, a good blue shade is obtained. Alkali blue finds its principal application in wool-dyeing.

Disulphonic Acid,

$C_{38}H_{29}N_3(SO_3H)_2$,

is a product of the further action of sulphuric acid on the above acid. It is soluble in pure water, but insoluble in dilute sulphuric acid, and may therefore be precipitated from the sulphuric-acid solution by water.

It forms two series of salts with bases—acid salts, which have a coppery reflex, and neutral salts, which are colourless. The acid sodium salt is a commercial product, and is known as "water blue for silk."

Tri- and Tetra-sulphonic Acids.

These bodies result by continued action of sulphuric acid at a higher temperature.

They are not precipitated from an acid solution by water, and thus differ from the disulphonic acid. In order to isolate them, the sulphuric-acid solution is neutralised with chalk, and the precipitated calcium sulphate filtered off. The solution of lime-salt is then converted into sodium-salt.

The dyestuff known as "soluble blue for cotton" is probably a mixture of both acids, or rather of their acid sodium-salts.

All the "soluble blues" are dyed on wool and silk from a bath containing sulphuric acid. Cotton is previously mordanted with alum and soap, or with tannin and tartar emetic.

Another blue is obtained by the action of aniline and benzoic acid on pararosaniline. This product is valued for the pure greenish shade which it produces, and it has recently found extensive application, and appears to have almost displaced diphenylamine blue.

Homologues of aniline blue have been prepared by the action of toluidines on rosaniline. They possess a dull reddish shade.

Naphthylrosanilines are formed by action of the naphthylamines on rosaniline, but, like the above, possess no technical interest.

Diphenylamine Blue.

Girard and Delaire (Jahresber. 1867, p. 695).

Dyestuffs of a very pure blue shade are formed by the action of oxalic acid or of hexachloride of carbon (C_2Cl_6) on diphenylamine. On a large scale diphenylamine blue is prepared by heating diphenylamine with oxalic acid to 110°–120°. The dyestuff formed, which amounts to only 10 per cent. of the diphenylamine employed, is purified by repeated treatment with alcohol. It comes into commerce in the form of its higher sulphonic acids (soluble blue), and finds its principal application in silk- and cotton-dyeing.

Similar dyestuffs, probably identical with diphenylamine blue, are formed by treating methyldiphenylamine with oxidising agents, as, for example, with chloranil [15].

A dyestuff named Bleu de Mulhouse was prepared by Gros-Renaud and Schaeffer by the action of alkaline shellac solution on rosaniline.

Persoz, Deluyne, and Calvetet obtained (1861) a soluble blue dyestuff by the action of anhydrous stannic chloride on aniline (pure ?). The composition of this compound is not known, neither has it been applied in practice [41].

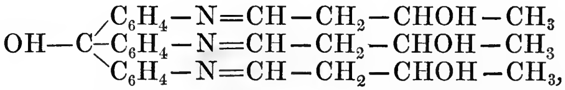
Aldehyde Green [43, 70, 71].

On treating rosaniline with aldehyde and sulphuric acid, a blue dyestuff is formed, which, on treatment with sodium thiosulphate in acid solution, yields aldehyde green. For its preparation, a mixture of rosaniline, aldehyde, and sulphuric acid is heated, till the product produces a blue-violet solution with water. It is then poured into a very dilute solution of sodium thiosulphate. Sulphur and a grey compound separate, while the green remains dissolved. It may be precipitated by addition of zinc chloride or acetate of soda; in one case a zinc double salt, and in the other a free base, is obtained.

The chemistry of the reactions taking place in the preparation of aldehyde green has been studied in detail with pararosaniline.

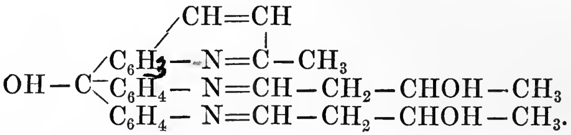
In the first stages of the reaction a blue dyestuff, the so-called aldehyde blue, is formed, along with a green dyestuff.

This blue has the composition of an anhydro-aldol-pararosaniline,

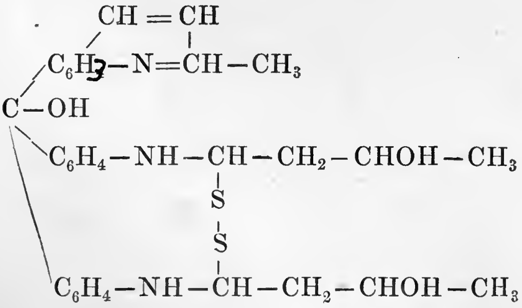


$$\mathrm{OH{-}C}\begin{cases}\mathrm{C_6H_4{-}N{=}CH{-}CH_2{-}CHOH{-}CH_3}\\ \mathrm{C_6H_4{-}N{=}CH{-}CH_2{-}CHOH{-}CH_3}\\ \mathrm{C_6H_4{-}N{=}CH{-}CH_2{-}CHOH{-}CH_3},\end{cases}$$

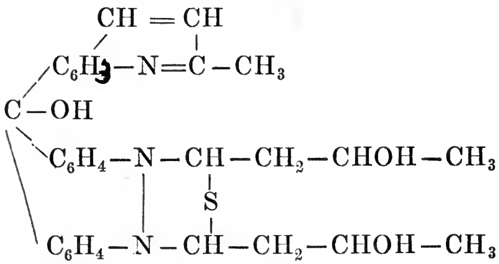
and is incapable of yielding the green on treatment with a thiosulphate. The green dyestuff formed at the same time is a quinaldine derivative of the above dyestuff, and has the constitution



The thiosulphate employed in the reaction enacts two functions. It separates the above blue dyestuff, and at the same time converts the green dyestuff into a new compound, containing sulphur, which is faster to light and dyes a better shade than the original green. Two processes were originally in vogue for the production of aldehyde green. The process of Lucius consists in treating the mixture obtained by the action of aldehyde and sulphuric acid on rosaniline with sulphuretted hydrogen and then with sulphurous acid, while in that of Usèbe the agent employed is a thiosulphate. The green dyestuffs obtained in these processes are both derived from the above green, but differ in composition. The green obtained in Lucius's process contains two atoms of sulphur, while that of Usèbe only contains one. Their constitutions are expressed by the following formulæ:—



Lucius's Green.



Usèbe's Green.

Of course, the products obtained from rosaniline contain one methyl-group more than is expressed in the above formulæ: its position can only be a matter of speculation.

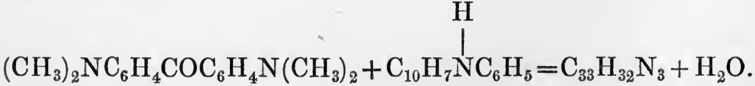
Aldehyde green is a basic dyestuff, and was largely used before the introduction of iodine green. The zinc double salt came into commerce as a paste, or the green was prepared by the consumers. The tannate, obtained by precipitating the solution with tannic acid, was used in printing, being used with acetic acid and fixed by steaming.

Diphenylnaphthylmethane Dyestuffs [1].

Certain derivatives of diphenylnaphthylmethane similar to the diphenylmethane derivatives already described are in use as dyestuffs.

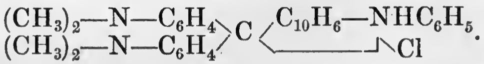
Compounds of this class are obtained by the action of substituted naphthylamines on tetramethyldiamidobenzophenone in presence of dehydrating agents. In place of the latter compound its chloride or the corresponding benzhydrol may be used.

Victoria Blue B is the product of the action of phenyl-α-naphthylamine on tetramethyldiamidobenzophenone in presence of phosphorus oxychloride. The reaction is expressed by the following equation:—



$$(CH_3)_2NC_6H_4COC_6H_4N(CH_3)_2 + C_{10}H_7\overset{\overset{H}{|}}{N}C_6H_5 = C_{33}H_{32}N_3 + H_2O.$$

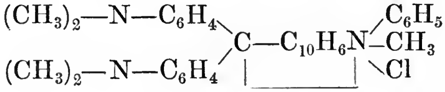
The constitution of the dyestuff is represented by the formula



$$\begin{matrix}(CH_3)_2-N-C_6H_4 \\ (CH_3)_2-N-C_6H_4\end{matrix}\!\!>C\!\!<\!\!\begin{matrix}C_{10}H_6-NHC_6H_5 \\ \llcorner\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\lrcorner Cl\end{matrix}.$$

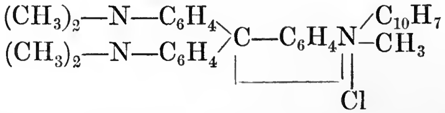
Victoria Blue 4 R.—This dyestuff is obtained by a similar process with methylphenyl-α-naphthylamine. Its constitution is expressed by one of the following formulæ, the second being the more probable, as it differs greatly in shade from Victoria Blue B.

I.



$$\left.\begin{array}{l}(CH_3)_2-N-C_6H_4\\(CH_3)_2-N-C_6H_4\end{array}\right>C-C_{10}H_6N\left<\begin{array}{l}C_6H_5\\CH_3\\Cl\end{array}\right.$$

II.



$$\left.\begin{array}{l}(CH_3)_2-N-C_6H_4\\(CH_3)_2-N-C_6H_4\end{array}\right>C-C_6H_4N\left<\begin{array}{l}C_{10}H_7\\CH_3\\Cl\end{array}\right.$$

Night Blue is obtained from paratolyl-α-naphthylamine ($p\text{-}C_7H_7NHC_{10}H_7$) and tetramethyldiamidobenzophenone. These dyestuffs come into commerce as hydrochlorides. They are beautiful blue dyestuffs, easily soluble, and dye cotton prepared with tannic acid similarly to methylene blue, but unfortunately the shades produced are not very fast to light. In general their reactions resemble those of the rosaniline dyestuffs. Alkalies precipitate a reddish-brown base, and acids turn the blue colour to yellow.

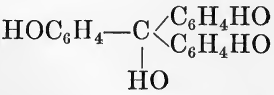
Victoria blue B base cannot be crystallised. In a pure state it forms a brick-red powder; M.P. 95°.

Victoria blue 4 R base has also not been obtained in a crystallised state. It resembles the above in appearance, and melts at 77° [72].

B. ROSOLIC ACID DYESTUFFS.

These dyestuffs are closely related to those obtained from rosaniline, and may be regarded as rosanilines in which the nitrogen is replaced by a group containing oxygen.

The actual dyestuffs, like rosaniline salts, are anhydrides of a carbinol. For example, aurin, $C_{19}H_{14}O_3$, is the anhydride of an unknown carbinol, trioxytriphenylcarbinol :—

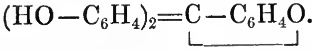


$$HOC_6H_4-\underset{\displaystyle HO}{\underset{|}{C}}\left<\begin{array}{l}C_6H_4HO\\C_6H_4HO\end{array}\right.$$

[12].

The compounds of these series have an acid character, and in the free state are yellow, while the salts dissolve in water with a red colour. They cannot be fixed on textile fibres, and are consequently almost useless in dyeing. Some of the colour-lakes are used in paper manufacture and for colouring tapestry.

Aurin, Pararosolic Acid [12].



$$(HO-C_6H_4)_2=\underbrace{C-C_6H_4O}_{}.$$

Aurin is prepared by heating phenol with oxalic acid and sulphuric acid: 6 parts of phenol, 3 parts sulphuric acid, and 4 parts of dried oxalic acid are heated for about twenty-four hours to 120°–130°.

The melt is extracted with water, and the residue dissolved in hot alcohol, and ammonia gas passed into the solution. The precipitate which forms is boiled with acetic acid or hydrochloric acid [44, 48, 49]. Aurin is also formed by condensation of phenol with formic acid and zinc chloride [45], by boiling the diazo-compound from pararosaniline with water [12], by heating dioxybenzophenone chloride with phenol [46], and by action of salicylic aldehyde on phenol in presence of concentrated sulphuric acid [47].

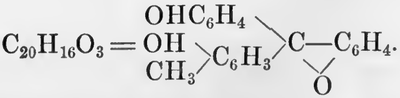
Aurin forms dark red rhombic crystals or red needles with a green metallic reflex. It decomposes without melting. It dissolves in alcohol and glacial acetic acid with a yellowish-red colour, and in alkalies with a magenta-red colour. It forms soluble double compounds with bisulphites of the alkalies.

$KHSO_3,C_{19}H_{14}O_3$ forms colourless leaflets, immediately decomposed by acids. Aurin further forms a very unstable compound with hydrochloric acid. Reducing agents convert aurin to leucaurin ($C_{19}H_{16}O_3$) (trioxytriphenylmethane). On heating with aqueous ammonia to 120° it yields pararosaniline [13].

It is decomposed by heating with water, phenol and dioxybenzophenone being produced.

For bye-products of aurin manufacture see the original article [49].

Rosolic Acid.



$$C_{20}H_{16}O_3 = \begin{matrix} OHC_6H_4 \searrow \\ \begin{matrix}OH\\CH_3\end{matrix}\rangle C_6H_3 \nearrow \end{matrix} C\underset{\diagdown O \diagup}{-}C_6H_4.$$

This body is formed on boiling the hexazo-compound of rosaniline ($C_{20}H_{19}N_3$) with water [50], and may be obtained by heating a mixture of phenol and cresol with arsenic acid and sulphuric acid [49].

The rosolic acid described by Runge (1834) as obtained from the residue of crude phenol distillation is probably identical with the body at present under consideration.

Rosolic acid forms infusible lustrous green crystals. It is almost insoluble in water, but dissolves easily in alcohol and acetic acid with an orange-red colour. Its alkaline solutions are red. It gives colourless double compounds with bisulphites, and in its general behaviour closely resembles aurin. On reduction, leucorosolic acid (trioxydiphenyltolylmethane), $C_{20}H_{18}O_3$, is formed. Dioxyphenyltolylketon and phenol are products of its decomposition with water [31].

Two other products obtained from aurin have also been used to some extent in practice.

Red coralline [52] or Peonine is obtained by heating crude aurin with ammonia under pressure, and is probably intermediate in composition between aurin and pararosaniline. Azulin is obtained by action of aniline on aurin, and is probably an aurin containing aniline groups [53]. This blue dyestuff was largely used before the introduction of aniline blue.

Pittacal (Eupittonic Acid).

The formation of this dyestuff was first observed by Reichenbach in 1835. He obtained it by treating certain fractions of beech-tar creosote with baryta-water in presence of air [54].

The formation of similar blue products has also been noticed by Graetzel, and the subject has been investigated by Liebermann and by A. W. Hofmann.

Liebermann gave to his product the name Eupitton or Eupittonic acid, but it is not certain that this body is identical with Reichenbach's Pittacal [55]. The constitution and method of formation of this body were determined by Hofmann [56].

Eupittonic Acid, Hexamethoxylaurin [55].

$$C_{19}H_8(OCH_3)_6O_3.$$

This compound is obtained by action of carbon hexachloride on an alkaline solution of two molecules of pyrogalloldimethyl ether and one molecule of methylpyrogalloldimethyl ether at 160°–170°. It is also formed by action of air on an alkaline solution of both ethers [56].

Eupittonic acid forms orange-yellow needles, insoluble in water and soluble in alcohol and ether. It is a dibasic acid and forms salts which have a blue colour in solution. They may be precipitated by an excess of alkali. The salts of the heavy metals are sparingly soluble blue lakes. Like aurin, eupittonic acid gives unstable compounds with acids.

Dimethyl ether [56], $C_{25}H_{24}O_9(CH_3)_2$, is formed by action of methyl iodide on the sodium salt. It forms golden-yellow needles. M.P. 242°.

Diethyl ether [56], $C_{25}H_{24}O_9(C_2H_5)_2$. M.P. 202°.

Diacetate [56], $C_{25}H_{24}O_9(C_2H_3O)_2$, yellow needles. M.P. 265°.

An analogous compound to eupittonic acid is obtained by oxidation of pyrogalloldimethyl ether with methylpyrogalloldimethyl ether—Tetraoxyethyldioxymethylaurin [56],

$$C_{19}H_8(OCH_3)_2(OC_2H_5)_4O_3.$$

This compound forms brick-red needles, soluble in ether.

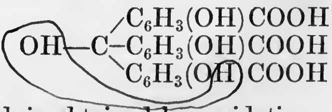
Hexamethoxylpararosaniline [25],

$$C_{25}H_{31}N_3O_7 = C_{19}H_{13}(OCH_3)_6N_3O,$$

is obtained by heating eupittonic acid with aqueous ammonia under pressure to 160°–170°. The formation of this body is analogous to that of pararosaniline from aurin. The base forms hair-like colourless needles, which rapidly become blue on exposure to the air. It is decomposed on heating with water, eupittonic acid being regenerated, while ammonia splits off.

The monoacid salts of this base are blue and the triacid yellow. The dyestuffs of this class are not of any technical value.

Aurintricarbonic Acid (CHROME-VIOLET) [73].

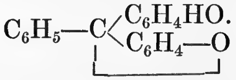


$$\mathrm{OH}-\mathrm{C}\left\{\begin{array}{l}\mathrm{C_6H_3(OH)COOH}\\ \mathrm{C_6H_3(OH)COOH}\\ \mathrm{C_6H_3(OH)COOH}\end{array}\right.$$

This compound is obtained by oxidation of salicylic acid and methyl alcohol in concentrated sulphuric acid solution with sodium nitrite. It forms a red powder with greenish reflex, and produces bright shades on metallic mordants. The chromium lake is fast to soap. For the methyl alcohol may be substituted formaldehyde or methylal, and homologous derivatives may be obtained by replacing the whole or molecular portions of the salicylic acid by β-cresotic acid.

Dyestuffs from Benzotrichloride and Phenols.

Benzotrichloride, according to Doebner [57], acts on phenols in a similar manner to dimethylaniline. The dyestuffs formed are related to rosolic acid in their constitution; they are derivatives of triphenylmethane and contain an oxygen atom linked to the methane-carbon atom and one benzene ring. Throughout, however, they contain one intact phenyl ring, the other two containing oxygen. The simplest member of the class is formed by interaction of two molecules of phenol and one molecule of benzotrichloride, and is called Benzaurin. Benzaurin stands in the same relation to dioxytriphenylmethane as aurin does to trioxytriphenylmethane. Its constitution is accordingly the following :—



$$C_6H_5-C\begin{array}{l}\diagup C_6H_4HO.\\ \diagdown C_6H_4-O\end{array}$$

Benzaurin forms hard lustrous crusts. It is insoluble in water, soluble in alcohol, ether, and glacial acetic acid, with a yellow colour. It dissolves in alkalies with a violet colour, and is precipitated from its alkaline solution by acids. It forms soluble double compounds with bisulphites.

Benzaurin dyes wool and silk yellow from an acid bath. It yields dioxytriphenylmethane on reduction. This compound crystallises from alcohol in yellowish needles.

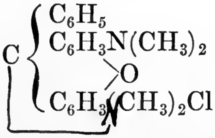
Resorcinbenzeïn, $C_{19}H_{14}O_4$, is an analogous body obtained by action of benzotrichloride on resorcin. With bromine it gives a tetrabrom-compound, which dyes silk a shade similar to that produced by eosine.

Basic derivatives of the above bodies have been recently described by Heumann and Rey [74].

These bodies, called Rosamines, are obtained by action of benzotrichloride on mono- or dialkyl derivatives of metamidophenol. The new bodies are beautiful red to violet dyestuffs.

One of the simplest members of the series—tetramethylrosamine—is prepared by heating one molecule benzotrichloride with two molecules dimethylmetamidophenol in benzene solution, or mixed with sand, to about 60°.

The hydrochloride forms needles with a steely-blue reflex, and dissolves easily in water with a beautiful bluish-red colour; the solution exhibits a bright yellowish-red fluorescence. Its constitution is expressed by the formula—



$$C\left\{\begin{array}{l} C_6H_5 \\ C_6H_3N(CH_3)_2 \\ \quad >O \\ C_6H_3N(CH_3)_2Cl \end{array}\right.$$

Tetramethylrosamine dyes wool and silk in an acid bath, producing shades from pink to dark bluish red.

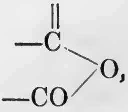
The oxalate forms dark green needles and the nitrate steel-blue needles.

By heating oxalic acid with resorcin and sulphuric acid, Baeyer obtained a yellow dyestuff, which is probably Euxanthone [58]. According to Claus and Andreæ [59] it possesses the formula $C_{13}H_8O_4$, while Gukassianz obtained two bodies in the same reaction, to both of which he ascribes the formula $C_{14}H_8O_5$ [60]. Rosicki [61] obtained a dyestuff by heating resorcin with isosuccinic acid and sulphuric acid. This body, Resorcin-isosuccineïn, has the same composition as Brasileïn, $C_{16}H_{14}O_5$, and is similar in its properties.

C. PHTHALEÏNS [62].

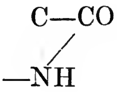
The phthaleïns are derivatives of triphenylmethane, and form a group of dyestuffs which are sharply defined from the rosaniline and rosolic acid derivatives already described. In the latter the chromophorous groups are in para positions, while in the former two adjacent positions are taken up.

The chromophor of the phthaleïns is the lacton ring :—

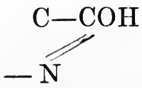


which occupies two adjacent positions in one benzene ring, one carbon atom being linked to another benzene ring.

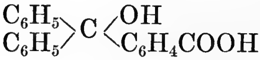
With respect to the colour-giving group, there is a certain analogy between these dyestuffs and those of the Indigo series, these latter being characterised by the lactam or lactim ring :—



or

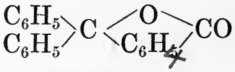


The phthaleïns are all derivatives of phthalophenone, the inner anhydride of triphenylcarbinolcarbonic acid :



$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>C<\!\begin{matrix}OH\\C_6H_4COOH\end{matrix}$$

Triphenylcarbinolcarbonic acid.



Phthalophenone.

This acid is not capable of existing in a free state, but may be obtained in form of its salts. The relationship between phthalophenone and triphenylmethane is easily determined. By treatment with alkalies it yields triphenylcarbinolcarbonic acid, and this may be converted to triphenylmethanecarbonic acid by reduction with zinc powder. On heating this latter compound, carbon dioxide splits off, forming triphenylmethane.

Phthalophenone is not a dyestuff, the tinctorial character only becoming apparent on introduction of hydroxyl groups into both phenyl groups.

The phthaleïns (hydroxylated phthalophenones) are almost exclusively obtained by action of phenols on phthalic anhydride.

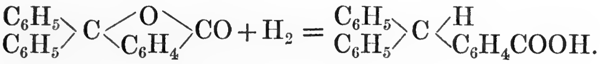
The position of the hydroxyl groups with reference to the methane carbon atom has considerable influence on the character of the dyestuff produced. With simple phenols, as, for example, in the formation of phenolphthaleïn, the hydroxyl group is in the para position to the carbon atom.

Compounds of this class are mostly of little character as dyestuffs. They are colourless and only form coloured salts. Real dyestuffs are only obtained from phenols which contain two hydroxyl groups in the meta position, such as resorcin and pyrogallol. Probably here also the condensation takes place in a para position to one hydroxyl group, and is therefore ortho to the other. The condensation is generally attended by the formation of an anhydride between two hydroxyl groups.

The phthaleïns, with exception of rhodamine, are acid dyestuffs.

The chromophor of the phthaleïns is of a strong acid character, and thus intensifies the acidity of the hydroxyl groups, and this effect may be considerably increased by introduction of halogens or nitro-groups into the benzene rings. The halogens exert considerable influence on the shade of the dyestuffs.

The coloured phthaleïns are converted into colourless phthalins on reduction, these latter bodies being the corresponding derivatives of triphenylmethanecarbonic acid.

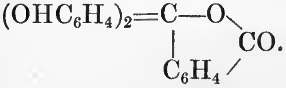


$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>C\!<\!\begin{matrix}O\\C_6H_4\end{matrix}\!>CO + H_2 = \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>C\!<\!\begin{matrix}H\\C_6H_4COOH.\end{matrix}$$

On treating with energetic dehydrating agents, most phthaleïns are converted into anthraquinone derivatives, one molecule of phenol being split off during the reaction [62].

The phthaleïns are very numerous, and only those of value from a technical or theoretical point of view are considered here.

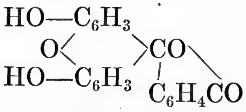
Phenolphthaleïn [62]. *Dioxyphthalophenone,*



$$\begin{array}{l}(OHC_6H_4)_2{=}C{-}O\diagdown\\ \qquad\qquad\quad\ |\qquad\quad CO.\\ \qquad\qquad C_6H_4\diagup\end{array}$$

This body is obtained by action of phenol on phthalic anhydride in presence of strong sulphuric acid. The free phthaleïn forms colourless crystals, melting at about 250°; it dissolves in alkalies with a red colour, and is precipitated by acids as a white precipitate. The alkaline solution is decolorised by excess of alkali. On melting with caustic potash, it yields benzoic acid and dioxybenzophenone. On account of the change in colour occasioned by free alkalies (not carbonate or ammonia), phenolphthaleïn is useful as an indicator in titration.

Fluoresceïn [62, 63].



(Inner anhydride of resorcinphthaleïn.)

Fluoresceïn is obtained by heating an intimate mixture of two molecules resorcin with one molecule phthalic anhydride to 190°–200°. The materials used in the manufacture should be as pure as possible, as impure fluoresceïn is difficult to purify. In the pure state it forms dark yellow crystals, sparingly soluble in alcohol, more easily in glacial acetic acid. It is almost entirely insoluble in water, but dissolves in alkalies, forming a yellowish-red solution, which, when dilute, exhibits a bright green fluorescence. Acids precipitate it from the alkaline solution as a yellow powder.

Corresponding chlorofluoresceïns are obtained by action of di- and tetra-chlorophthalic anhydride on resorcin. These compounds are entirely different from those formed by direct chlorination of fluoresceïn. In these the chlorine (bromine, or iodine) always enters the resorcin-rest. The fluoresceïns from the chlorinated phthalic acids serve as starting-points for a series of very brilliant phthaleïn dyestuffs, which were first introduced into the colour-industry by E. Noelting.

The chlorinated fluoresceïns have a somewhat redder shade than the corresponding fluoresceïns which contain no chlorine.

Eosin.

On treating fluoresceïn with bromine, substitution of the hydrogen atoms in the resorcin-rests takes place. The final result is that four hydrogen atoms of the fluoresceïn are replaced by bromine, the product being tetrabromfluoresceïn, $C_{20}H_8O_5Br_4$ [63].

The latter, and also the lower brominated products are beautiful red dyestuffs, the shade being yellower with less, and bluer with more, bromine. Pure tetrabromfluoresceïn [63] crystallises from alcohol in yellowish-red crystals, containing alcohol. It is almost insoluble in water, but forms easily soluble salts with alkalies, which exhibit a beautiful green fluorescence in solution.

From the alkaline solution, acids precipitate the colour-acid as a yellowish-red precipitate. The salts are only incompletely decomposed by acetic acid.

The lead, zinc, alumina, &c., salts are finely coloured insoluble lakes.

Tetrabromfluoresceïn and the lower brominated products come into commerce as sodium or potassium salts, and form the various brands of soluble eosins.

On wool and silk they are dyed from a slightly acid bath and produce brilliant shades of red. Those on silk are noteworthy for their peculiar yellowish-red fluorescence.

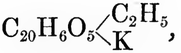
Two of the four bromine atoms are contained in each resorcin group, and on melting with potash eosin splits up into phthalic acid and dibromresorcin [64]. The bromine may be removed by nascent hydrogen; on reduction with sodium amalgam colourless fluorescin, $C_{20}H_{14}O_5$, is formed, and yields fluoresceïn on oxidation. Various methods have been proposed for the bromination of fluoresceïn on a large scale. For example, an alkaline fluoresceïn solution is mixed with the calculated amount of bromine dissolved in alkali, and on adding acid the fluoresceïn and bromine are liberated simultaneously and combination is thus effected. This process does not, however, appear to be successful, and at present bromination is carried out in alcoholic solution. Fluoresceïn in a finely divided state is suspended in alcohol, and the requisite amount of bromine added, the mixture being carefully cooled. The hydrobromic acid developed during the reaction is utilised by addition of potassium chlorate, which again liberates the bromine. In this manner a saving of bromine is effected, and only four atoms are necessary, while under ordinary conditions eight atoms are required, four being lost as hydrobromic acid.

Ethers of Eosins [63].

By treating the potassium salt of eosin with methyl iodide or chloride, or with ethyl bromide, monomethyl- and monoethyl-ethers of eosin may be obtained, and these even surpass the eosins in brilliancy of shade, their tone being in general somewhat bluer.

They are monobasic acids, as one unaltered hydroxyl group is present. The salts are insoluble in water and absolute alcohol, but dissolve with tolerable ease in alcohol of 50 per cent. The solutions show a magnificent fluorescence.

The potassium salt of monoethyltetrabromfluoresceïn,



$$C_{20}H_6O_5<\begin{matrix}C_2H_5\\K\end{matrix},$$

forms large ruby-red crystals with a fine green reflex.

The ethyl ether, in form of its sodium or potassium salt, is extensively used in silk-dyeing as spirit eosin or "primerose à l'alcool." For use, the commercial product is dissolved in spirit and gradually added to the dye-bath, which is acidified with acetic acid.

Colourless ethers of eosin also exist, and may be prepared by heating the silver salt of eosin with alcoholic iodides [63].

Iodine Derivatives of Fluoresceïn.

The commercial products known as "erythrosin" are iodine derivatives of fluoresceïn corresponding to eosins. The alkali-salts, which are the commercial products, are soluble in water, and possess a much bluer tone than the corresponding eosins, and their solutions do not exhibit the fluorescence characteristic of the latter bodies.

The commercial brands of erythrosin are of various marks, according to the amount of iodine they contain. On cotton they may be fixed in form of an insoluble alumina lake, and on this account are used somewhat extensively in cotton-dyeing, and also to a certain extent in colouring paper.

Dinitrodibromfluoresceïn.

$C_{20}H_8Br_2(NO_2)_2O_5$ [62].

This dyestuff is formed by bromination of dinitrofluoresceïn or by nitration of di- or tetrabromfluoresceïn. On a large scale it is prepared by treating dibromfluoresceïn with nitric acid in alcoholic solution. Pure dinitrodibromfluoresceïn forms yellow needles, sparingly soluble in alcohol and acetic acid. It is a strong dibasic acid, and forms easily soluble salts with alkalies. The solutions of its salts are yellow if concentrated, red if dilute, and do not fluoresce.

The sodium salt is known in commerce as Eosin Scarlet, Safrosin, or Lutecienne.

It produces a beautiful bluish-red shade on wool, and may be used in conjunction with yellow dyestuffs, giving fine scarlet tones. Its application in wool-dyeing has fallen off considerably since the introduction of the red azo-dyes.

Tetrabromdichlorfluoresceïn.

$C_{20}H_6Cl_2Br_5O_5$.

Tetrabromtetrachlorfluoresceïn.

$C_{20}H_4Cl_4Br_4O_5$.

These bodies are prepared in a similar manner to the eosines, by bromination of the di- and tetra-chlorfluoresceïn. The soluble alkali-salts of these acids are brought into commerce as the various brands of Phloxin.

Their ethyl ethers, which, like those of eosin, are soluble in dilute alcohol, are known commercially as Cyanosin. Iodine derivatives of di- and tetra-chlorfluoresceïn form the principal constituents of the dyestuff known as Rose Bengal.

The fluoresceïn derivatives containing chlorine are much bluer in shade than the corresponding derivatives of ordinary fluoresceïn. Their principal application is in silk-dyeing. Rose Bengal prepared from tetrachlorphthalic acid is the bluest of these dyestuffs, while Phloxin from dichlorphthalic acid is the yellowest.

Here again the shade may be varied at will by introduction of more or less iodine or bromine.

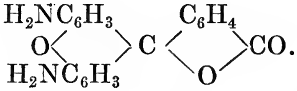
Rhodamine [75].

The phthaleïns of metamidophenol and its derivatives have been introduced into commerce under the above name. These dyestuffs are characterised by the brilliancy of the shades which they are capable of producing, in fact excelling in beauty all other red dyestuffs.

Commercial rhodamine consists principally of the phthaleïn of diethylmetamidophenol. The condensation of metamidophenol (and its derivatives) with phthalic anhydride only takes place in presence of strong sulphuric acid.

Rhodamines may also be prepared by action of dimethyl- or diethylamine on the chloride formed on treating fluoresceïn with phosphorus oxychloride.

The constitution of the simplest rhodamine is probably analogous to that of fluoresceïn, and is expressed by the formula :—



$$O\left\langle\begin{matrix}H_2NC_6H_3\\ H_2NC_6H_3\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_4\\ O\end{matrix}\right\rangle CO.$$

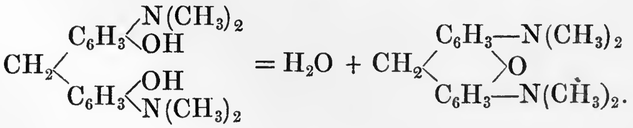
Unlike the ordinary phthaleïns, rhodamine possesses basic and acid properties. It forms soluble salts, from which the base is not separated by alkalies. The solutions are turned yellow by an excess of mineral acid.

The shade of rhodamine is a magnificent red, and exhibits on silk a hitherto unrivalled fluorescence.

More recently the condensation-product of succinic acid and dimethylmetamidophenol has been prepared on a large scale and sold as Rhodamine S. It is especially adapted for cotton-dyeing.

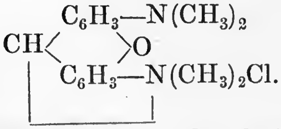
Pyronines [76].

The Pyronines are a series of red basic dyestuffs of comparatively recent introduction. They are derivatives of diphenylmethane, and resemble the rhodamines in shade. A typical pyronine may be prepared as follows :—Dimethylmetamidophenol is condensed with formaldehyde, and the resulting dioxytetramethyldiamidodiphenylmethane is treated with strong sulphuric acid, whereby one molecule of water is split off, and a leuco-base, tetramethyldiamidodiphenylmethane-oxide, is formed, according to the equation :—



$$CH_2\left\langle\begin{matrix}C_6H_3\left\langle\begin{matrix}N(CH_3)_2\\ OH\end{matrix}\right.\\ C_6H_3\left\langle\begin{matrix}OH\\ N(CH_3)_2\end{matrix}\right.\end{matrix}\right. = H_2O + CH_2\left\langle\begin{matrix}C_6H_3—N(CH_3)_2\\ C_6H_3—N(CH_3)_2.\end{matrix}\right\rangle O$$

From this the dyestuff (Pyronine G) is obtained by oxidation. It has the formula :—



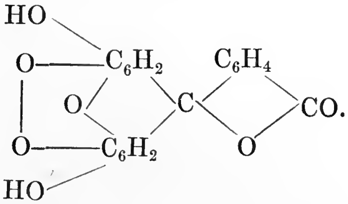
$$CH\left\langle\begin{matrix}C_6H_3—N(CH_3)_2\\ C_6H_3—N(CH_3)_2Cl.\end{matrix}\right\rangle O$$

Pyronine B is the corresponding ethyl derivative.

The pyronines yield brilliant bluish-red shades on cotton mordanted with tannic acid.

Galleïn and Cœruleïn [65].

Galleïn.—The first product of the interaction of phthalic anhydride and pyrogallol is a phthaleïn anhydride analogous to fluoresceïn, which, however, undergoes further oxidation by the air, two hydroxyl groups being converted to quinone groups. The galleïn thus formed possesses the formula—



It differs from fluoresceïn in containing two quinone oxygen atoms in combination with two benzene rings.

Galleïn is generally prepared by heating phthalic anhydride with gallic acid to 200°. The latter is converted into pyrogallol at this temperature, carbonic acid being split off.

In the pure state galleïn forms brilliant green crystals or a brownish-red powder, easily soluble in alcohol with a dark red colour, and difficultly soluble in ether.

The salts with the alkalies, lime, and baryta are soluble in water with a red colour, which is turned blue by an excess of alkali. On reduction, it is converted to hydrogalleïn and, finally, to gallin. It forms greyish-violet lakes with alumina and chromic oxide. It produces a fine violet on wool mordanted with bichromate.

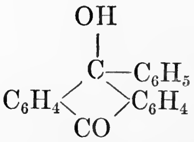
In printing it is applied with acetate of aluminium or chromium and steamed, whereby acetic acid is liberated, and the aluminium or chromium lake of galleïn is fixed on the fibre.

Cœruleïn [65], $C_{20}H_8O_6$, is formed by heating galleïn with twenty times its weight of concentrated sulphuric acid to 200°. The dyestuff is precipitated by water, and in this state forms a bluish-black powder, which takes a metallic lustre on rubbing. It is almost insoluble in water, alcohol, and ether, slightly soluble in glacial acetic acid with a green colour, and easily in concentrated sulphuric acid with an olive-green colour. It forms a blue solution with hot aniline.

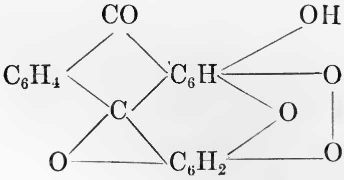
It crystallises from hot concentrated sulphuric acid in warty crystals. Reducing-agents convert it to reddish-brown cœrulin, $C_{20}H_{12}O_6$. On warming with acetic anhydride, a triacetylcœruleïn, $C_{20}H_9O_6(C_2H_3O)_3$, is formed. Cœruleïn forms colourless soluble compounds with bisulphites; these compounds being easily decomposed by boiling or by action of alkalies or acids. In dyeing and printing the bisulphite compound is generally used. For printing, the cœruleïn bisulphite compound (Cœruleïn S) is mixed with aluminium or chromium acetate, printed, and steamed. This decomposes the acetate and the bisulphite compound simultaneously, and cœruleïn becomes fixed as aluminium or chromium lake. Wool is previously mordanted with bichromate and tartar.

The shades produced are dark green, not very bright, but useful on account of their great fastness.

On distilling with zinc powder, cœruleïn gives phenylanthracene, and, according to Buchka, is a derivative of phenyloxanthranol :—



The constitution of cœruleïn is expressed by the following formula :—



[66].

Glycereïns [67].

Reichl gives this name to a series of coloured products obtained by action of phenols on glycerin in presence of concentrated sulphuric acid. The quantity of dyestuff formed is, however, so small that one can scarcely formulate any reaction in form of an equation.

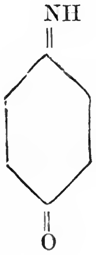
Similar bodies to these from glycerin are also obtained from many organic acids, alcohols, and sugars.

CHAPTER VI.

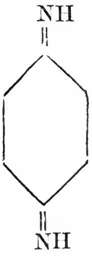
QUINONEIMIDE DYESTUFFS.

The dyestuffs comprised under this head are derivatives of the hitherto unknown imido-compounds of the quinones, and include, amongst others, the Indamines and Indophenols.

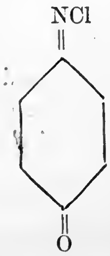
By replacing the oxygen atoms of quinone by the divalent group NH, the following compounds are obtained, according as the substitution takes place once or twice.



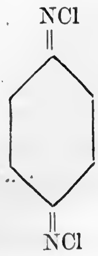
and



These compounds are unknown in the free state. Various derivatives are, however, known, amongst the simplest of which may be mentioned quinonechlorimide and quinonedichlordiimide.



Quinonechlorimide.

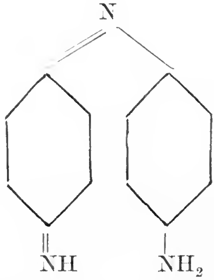


Quinonedichlordiimide.

The above-mentioned indamines and indophenols must be regarded as more complex derivatives of the quinoneimides.

These dyestuffs are formed by oxidation of a paradiamine in presence of a monamine or a phenol, or by action of quinonedichlordiimide on the latter.

In the oxidation process, as, for example, that of paraphenylenediamine with aniline, the former is probably converted into quinonediimide $HN{=}C_6H_4{=}NH$, which, on further oxidation attacks the benzene chain of the aniline, and enters in the para position to the amido-group. The indamine produced has the constitution [1]:



This constitutional formula is deduced from the following facts:—On reduction the compound takes up two atoms of hydrogen, forming paradiamidodiphenylamine:—

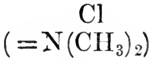
$$H_2N—C_6H_4—NH—C_6H_4—NH_2.$$

As the indamine may be reproduced on oxidation, this body must be regarded as the leuco-base of the dyestuff. That the nitrogen atom effecting the linkage in the indamine is tertiary is seen from the fact that a paradiamine substituted in both amido-groups, as, for example, diethylparaphenylenediamine,

$$C_2H_5—HN—C_6H_4—NH—C_2H_5,$$

is incapable of forming an indamine. That the nitrogen atom effecting the linkage in the indamines occupies the para position to the amido-group is easily proved, as paradiamines do not react with para substituted monamines, or at least only in a different manner.

Para-diamines substituted in one amido-group react like primary amines, and the monamine may also be secondary or tertiary. In many such cases the formation of an ammonium-chloride group

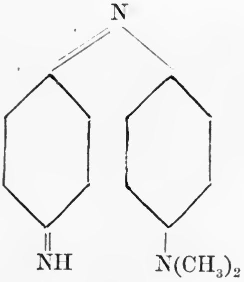


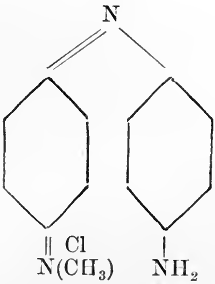
$$\overset{Cl}{(=N(CH_3)_2)}$$

has to be assumed.

The behaviour of certain tertiary indamines shows that their production is attended by an intermediate formation of a quinoneimide. If, on the one hand, paraphenylenediamine is oxidised with dimethylaniline, and, on the other, unsymmetrical dimethylparaphenylenediamine [$(CH_3)_2NC_6H_4NH_2$] with aniline, indamines are formed in both cases, but are not identical with each other, but isomeric, as by further action of aniline they yield two different dimethylsaffranines.

This behaviour is easily explained under the following assumptions :—Paraphenylenediamine yields first the body $HN—C_6H_4—NH$; while from dimethylphenylenediamine the chlormethylate, $Cl(CH_3)_2N—C_6H_4—NH$, is produced. The further action of these compounds on the respective monamines must necessarily produce different indamines, the constitution of which is expressed by the following formulæ :—





It is not improbable that the red dyestuff obtained by Wurster by oxidation of dimethylparaphenylenediamine is none other than the chlormethylate of methylquinoneimide :—

$$Cl(CH_3)_2\equiv N=C_6H_4NH.$$

This compound yields dimethylphenylenediamine on reduction, and reacts with monamines and phenols to produce indamines and indophenols.

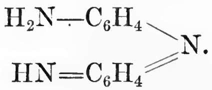
The indophenols are related to the analogues of oxyamidodiphenylamine in the same manner as the indamines are to diamidodiphenylamine.

The formation of dyestuffs by oxidation of paradiamines with monamines was first discovered by R. Nietzki [48] in 1879, who later [1] determined the constitution of the indamines. Witt, in 1879, discovered the reaction between nitrosodimethylaniline and amines and phenols.

Bernthsen [36] showed later that certain dyestuffs containing sulphur (methylene blue and Lauth's violet) also belong to this class of colouring-matters.

1. INDAMINES.

Indamine (Phenylene Blue) [1].

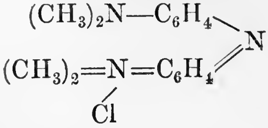


$$\left.\begin{array}{l}H_2N-C_6H_4\\HN=C_6H_4\end{array}\right\rangle N.$$

This compound is formed by oxidation of p-diamidodiphenylamine, or of a mixture of equal molecules of paraphenylenediamine and aniline. It is the simplest member of the indamine series, and its salts are greenish blue and are mostly soluble in water. Acids turn the solutions green, and rapid decomposition, with formation of quinone, sets in. The iodide separates in long brilliant green crystals from a mixture of the hydrochloride and potassium iodide. Indamine, on reduction, yields paradiamidodiphenylamine. On heating with a solution of an aniline-salt, phenosaffranine is formed.

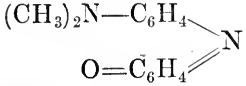
Tetramethylindamine [1, 2, 3].

(Bindschedler's Green.)



$$\left.\begin{array}{l}(CH_3)_2N-C_6H_4\\(CH_3)_2=\underset{\diagup Cl}{N}=C_6H_4\end{array}\right\rangle N$$

This compound is obtained by oxidation of equal molecules of dimethylparaphenylenediamine and dimethylaniline [1, 2, 3]. The solutions of the salts have a fine green colour, which is turned blue by alkalies. If the action of the latter is protracted, dimethylamine is evolved, and probably an indophenol



is formed. This indamine is in general more stable than the former one, but is decomposed on warming with acids, quinone and dimethylaniline being formed.

It yields tetramethyldiamidodiphenylamine [1] on reduction.

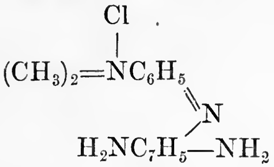
Iodide, $C_{16}H_{20}N_3I$ [1], is formed on addition of potassium iodide to a solution of the hydrochloride or zinc double salt, and separates in long green needles. It is pretty soluble in pure water, but insoluble in a solution of potassium iodide.

Zinc double salt [2, 3], $(C_{16}H_{20}N_3Cl)_2,ZnCl_2$, forms coppery needles, which are easily soluble in water.

Mercury double salt, $(C_{16}H_{20}N_3Cl)_2,HgCl_2$.

Platinum double salt, $C_{16}H_{20}N_3Cl_2,PtCl_4$.

Toluylene Blue [1, 4].

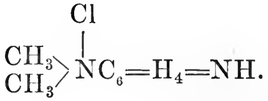


Toluylene blue may be obtained by mixing solutions of equivalent quantities of nitrosodimethylaniline hydrochloride and metatoluylenediamine, and also by oxidation of the latter base with dimethylparaphenylenediamine. It is an amido-indamine characterised by a greater degree of stability than the previous ones. The monoacid salts are blue, and the diacid salts are colourless.

The hydrochloride, $C_{15}H_{12}N_4,HCl$, forms soluble needles which possess a coppery lustre.

On reduction, toluylene blue gives triamidotolylphenylamine. On heating, toluylene red [4] (*see* Azine Dyestuffs) is formed.

The red dyestuff obtained by Wurster by oxidation of dimethylparaphenylenediamine is probably closely related to the indamines [5]. According to Wurster and Sendtner, this compound corresponds to a base of the formula $C_8H_{10}N_2$. It possesses the remarkable property of reacting with amines and phenols to produce indamines and indophenols respectively. It is possible that this compound is a methylate of methylquinone-diimide of the constitution—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\overset{Cl}{\overset{|}{N}}C_6{=}H_4{=}NH.$$

Tetramethylparaphenylenediamine gives a blue dyestuff, $C_{10}H_{14}N_2$, on oxidation.

2. INDOPHENOLS [7, 8, 12].

This series of dyestuffs, which were first prepared by Witt and Koechlin, by simultaneous oxidation of paradiamines or para-amidophenols with phenols, exhibit, both as regards constitution and general behaviour, a close relationship to the indamines. Like the latter, they are decomposed by acids with formation of a quinone. In general they possess a weak basic nature, but, unlike the indamines, form colourless salts, and have mostly a blue or violet colour in the free state.

On reduction they yield analogues of paramido-oxydiphenylamine.

Indophenols may be obtained by oxidation of paradiamines with phenols, or by action of nitrosodimethylaniline or quinonechlorimide on the latter class of compounds.

According to the above remarks the constitution of the simplest indophenol (from paraphenylenediamine and phenol) should be expressed by the formula,

$$HN{=}C_6H_4{=}N{-}C_6H_4{-}OH\,;$$

but the properties of the compounds of this class agree better with the formula—

$$O{=}C_6H_4{=}N{-}C_6H_4{-}NH_2.$$

For example, the indophenols do not possess acid properties, as might be expected if an hydroxyl group were present; on the contrary, they are weak bases.

The leuco-compounds, however, possess decided phenolic properties. They are soluble in alkalies, but oxidise extremely readily in the air, indophenols being formed, which, being insoluble in alkalies, separate out. In presence of acid the leuco-indophenols are stable in the air.

The application of these dyestuffs in dyeing and printing is based on the above properties of the leuco-compounds. The process is similar to indigo vat-dyeing. The goods are impregnated with an alkaline solution of the leuco-compound, the colour being developed by oxidation in the air, or by passing through a bath of potassium bichromate. Indophenol may also be produced directly on the fibre, a mixture of the diamine and phenol being applied, and the dyestuff developed by passing through bichromate or bleaching-powder solution.

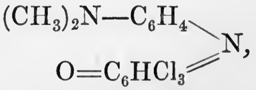
Only the indophenols from dimethylparaphenylenediamine and *a*-naphthol and phenol have been found capable of technical application.

The former compound is of an indigo-blue colour, and crystallises from benzene in brilliant green needles. It forms a colourless solution with acids; an excess decomposes it with formation of *a*-naphthaquinone and dimethylparaphenylenediamine [12]. The dyestuff from phenol is greenish blue.

The manufacture of the indophenols is effected by oxidation of an alkaline solution of the reacting compounds with sodium hypochlorite, or with air in presence of copper oxide. An interesting method of obtaining indophenol is by the action of dibrom-*a*-naphthol on dimethylparaphenylenediamine.

The indophenols are very fast to soap and light; their great sensitiveness towards acids and certain difficulties encountered in their application, however, render them unable to compete with indigo. Indophenol, however, appears to be of use when combined with indigo, *i.e.* when a vat of the mixed dyestuffs is used. It is claimed that this mixed vat is more economical than the simple indigo vat, while the fastness and beauty of the shades are not affected.

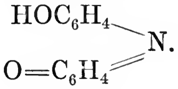
A *trichlorindophenol*,



$$\begin{matrix}(CH_3)_2N-C_6H_4\diagdown \\ \qquad\qquad\qquad\qquad N, \\ O=C_6HCl_3\diagup\!\!\diagup\end{matrix}$$

has been obtained by Schmitt and Andresen [10] by action of trichlorquinonechlorimide on dimethylaniline. It forms beautiful green needles.

Dyestuffs may also be produced by action of quinonechlorimide and of nitrosophenol on phenols in alkaline solution. They are, however, very unstable, and probably contain an hydroxyl group in place of the amido-group in the previously described indophenols. The simplest of these compounds would possess the formula :—

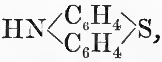


$$\left.\begin{array}{l}HOC_6H_4-\\O=C_6H_4=\end{array}\right\rangle N.$$

3. INDAMINES AND INDOPHENOLS CONTAINING SULPHUR.

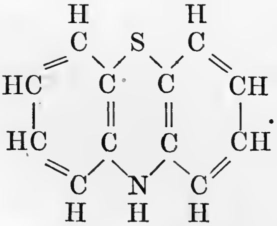
(THIAZINES.)

This class comprises a series of dyestuffs corresponding to the indamines and indophenols, but which contain one atom of sulphur in their molecule. This sulphur atom effects a linkage between two benzene rings, and the indamines of this series stand in the same relationship to thiodiphenylamine,



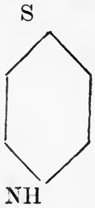
$$HN\left\langle\begin{array}{c}C_6H_4\\C_6H_4\end{array}\right\rangle S,$$

as the common indamines do to diphenylamine. The sulphur atom enters the two benzene chains in the ortho position to the imido-group, and accordingly thiodiphenylamine may be regarded as containing three rings each containing six members. This is exemplified by the following formula [36]:—

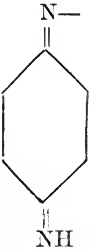


The amido and hydroxyl derivatives of thiodiphenylamine are, like those of diphenylamine, leuco-compounds.

There is an erroneous impression that the group



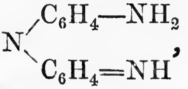
acts as chromophor, and that thiodiphenylamine is the chromogen of this class of dyestuffs. From Bernthsen's constitutional formulæ, however, these bodies belong to the Indamine group, and their chromophor must be the paraquinonediimide group—



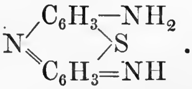
This is evident from the fact that the amido derivatives of thiodiphenylamine are not dyestuffs, but leuco-compounds. The presence of the sulphur atom serves to give greater stability to the molecule, and these bodies are stable to acids.

In general, the whole character of the series is considerably modified.

The simplest indamine,



corresponds to Lauth's Violet :

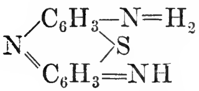


In this series also the nitrogenous groups are generally in the para position to each other.

The sulphuretted indamines may be produced by introduction of amido groups into thiodiphenylamine, and oxidation of the resulting leuco-compounds. They are generally prepared, however, by a peculiar reaction discovered by Lauth [14]. If a paradiamine is oxidised in presence of sulphuretted hydrogen in acid solution, one atom of nitrogen splits off as ammonia, and two molecules of the diamine combine, one atom of sulphur entering into both rests simultaneously. The resulting body is an indamine containing sulphur. These compounds are also formed on oxidation of thio derivatives of paradiamines. Small quantities are further obtained by oxidation of amidodiphenylamines in presence of sulphuretted hydrogen.

These dyestuffs are far more stable than the indamines and indophenols, and, unlike these, do not give quinone when treated with acid. For this reason they are capable of practical application, one of them, methylene blue, discovered by Caro, being used on a very large scale. The dyestuffs of this class have a violet or blue shade.

Lauth's Violet (*Thionine*) [14, 36].



is formed by oxidation of paraphenylenediamine hydrochloride in presence of sulphuretted hydrogen, by fusing paraphenylenediamine with sulphur and oxidising the resulting compound, and finally by oxidation of paradiamidothiodiphenylamine.

The base, $C_{12}H_9N_3S$, forms a black crystalline powder or needles with a greenish reflex. It dissolves in alcohol, forming a reddish-violet solution, and in ether, forming an orange solution.

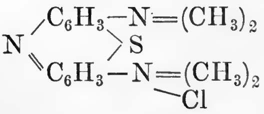
Hydrochloride, $C_{12}H_9N_3S,HCl$, forms beetle-green needles, soluble in water with a violet colour.

Hydriodide, $C_{12}H_9N_3S,HI$, is sparingly soluble in water [36].

Lauth's Violet gives a green solution with concentrated sulphuric acid, and on dilution the colour changes through blue to violet. On reduction it yields paradiamidothiodiphenylamine [36].

Isothionine is an isomeric dyestuff formed by oxidation of a diamidothiodiphenylamine of unknown constitution [36].

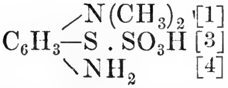
Methylene Blue [13, 15, 16, 36, 53].



This dyestuff was discovered by Caro, who obtained it by oxidation of dimethylparaphenylenediamine in presence of sulphuretted hydrogen.

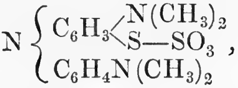
The dimethylparaphenylenediamine used in this and other processes is prepared by reduction of nitrosodimethylaniline, obtained by action of nitrous acid on dimethylaniline.

Caro's process was formerly used on an industrial scale. A considerable improvement was effected by oxidising equivalent quantities of dimethylparaphenylenediamine and dimethylaniline in presence of thiosulphuric acid. The most recent processes have for their starting-point dimethylparaphenylenediamine-thiosulphonic acid :



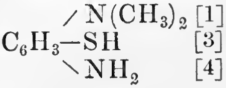
$$C_6H_3\begin{array}{ll} \diagup N(CH_3)_2 & [1] \\ -S\,.\,SO_3H & [3] \\ \diagdown NH_2 & [4] \end{array}$$

This compound is obtained by oxidation of dimethylparaphenylenediamine in presence of sodium hyposulphite, or by action of hyposulphurous acid (thiosulphuric acid, $H_2S_2O_3$) on the red oxidation product of dimethylparaphenylenediamine. Two processes may be employed for the manufacture of methylene blue from this compound. (1) The thiosulphonic acid is oxidised with dimethylaniline, whereby an insoluble compound :



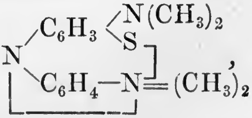
$$N\begin{cases} C_6H_3\begin{array}{l} \diagup N(CH_3)_2 \\ \diagdown S-SO_3 \end{array} \\ C_6H_4N(CH_3)_2 \end{cases},$$

tetramethylindamine-thiosulphonate, is formed. On boiling with zinc-chloride solution, it yields sulphuric acid and leucomethylene blue, which is converted into the dyestuff on oxidation. (2) On reduction, the thiosulphonic acid yields dimethylparaphenylenediamine mercaptan—



$$C_6H_3\begin{array}{ll} \diagup N(CH_3)_2 & [1] \\ -SH & [3] \\ \diagdown NH_2 & [4] \end{array}$$

or, on treating with acids, the corresponding disulphide $(C_8H_{11}N_2S)_2$. On oxidation with dimethylaniline, both these compounds give the same soluble green indamine :



tetramethylindamine sulphide, which is transformed to leucomethylene blue and methylene blue on standing or on warming the solution. Small quantities of methylene blue are formed by oxidation of tetramethyldiamidodiphenylamine in presence of sulphuretted hydrogen, and by treating tetramethylindamine with sulphuretted hydrogen.

Another method used in the manufacture of the so-called ethylene blue consists in treating nitrosodimethylaniline in sulphuric acid solution (sp. gr. 1·4) with zinc sulphide. Leuco-methylene blue is produced, and yields the dyestuff on oxidation.

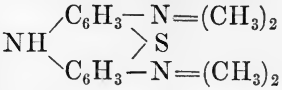
It is certain that methylene blue is the tetramethyl derivative of Lauth's violet, although it cannot be obtained by direct methylation of the latter. Its constitution is analogous to that of tetramethylindamine. Like this, it contains a pentavalent nitrogen atom, which is in combination with two methyl groups and an hydroxyl or acid radical. The hydrochloride has the constitution expressed at the head of the section. The properties of the base of methylene blue are those of an ammonium base, and this agrees with the above conception of its constitution. The base is not easily separated from its salts. It is best obtained by decomposition of the hydrochloride with silver oxide, and has probably the formula $C_{16}H_{18}N_3SOH$. It dissolves easily in water with a blue colour.

Hydrochloride, $C_{16}H_{18}N_3SCl$, forms small lustrous leaflets, easily soluble in water.

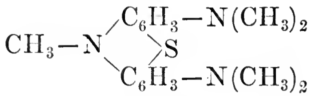
Zinc double salt, $2(C_{16}H_{18}N_3SCl) + ZnCl_2 + H_2O$ (commercial methylene blue), forms coppery needles, easily soluble in water, sparingly soluble in zinc chloride solution.

Hydriodide, $C_{16}H_{18}N_3SI$, forms lustrous brown needles, sparingly soluble in water.

Concentrated sulphuric acid dissolves methylene blue with a green colour. Reducing agents convert it to its leuco-derivative, tetramethyldiamidothiodiphenylamine—



This base forms colourless leaflets, which oxidise in the air to methylene blue. On treating with methyl iodide, the dimethyliodide of pentamethyldiamidothiodiphenylamine—



$$CH_3{-}N\begin{cases}C_6H_3{-}N(CH_3)_2\\ \quad\quad >S\\ C_6H_3{-}N(CH_3)_2\end{cases}$$

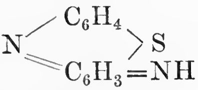
is formed.

As this compound is also formed by methylation of the leuco-compound of Lauth's violet, the relationship between the two dyestuffs is demonstrated.

Like most ammonium bases, methylene blue does not dye wool easily, but is readily fixed on silk and tannined cotton. It has also a slight affinity for unmordanted vegetable fibres. Methylene blue is principally used in cotton-dyeing. It dyes a greenish shade of blue, which shows a dull tone similar to that of indigo. It is very fast to light, and the shades may be readily modified by other basic dyestuffs, such as methyl violet or malachite-green.

An analogous dyestuff to methylene blue is obtained from monoethylparaphenylenediamine [Oehler, 20], and another from methoxydimethylparaphenylenediamine [Mülhauser, 21].

Imidothiodiphenylimide [36].



$$N\begin{cases}C_6H_4\\ \quad\quad >S\\ C_6H_3{=}NH\end{cases}$$

This body contains one amido group less than Lauth's violet, and is formed by oxidation of monamidothiodiphenylamine.

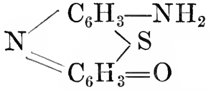
The base forms small reddish-brown needles, soluble in alcohol and ether with the same colour.

Hydrochloride, $C_{12}H_8N_2S,HCl+1\frac{1}{2}H_2O$, forms a brown precipitate insoluble in ether. It dissolves in water with blue-violet colour, and gives a green solution with concentrated sulphuric acid. The zinc-chloride double salt, $(C_{12}H_8N_2S,HCl)_2ZnCl_2$, forms long brownish-violet needles.

The compounds hitherto described correspond to the indamines; the following ones must be regarded as sulphuretted indophenols, as oxygen partly takes the place of the nitrogenous groups of the former.

The influence of the sulphur atom in adding to the stability of the molecule is also very apparent in these bodies, as they exhibit a far greater resistance to the action of chemical agents than the corresponding simple indophenols.

Thionoline (*Thioxindophenol*) [36].



This compound may be obtained by oxidation of paramidophenol in presence of sulphuretted hydrogen, or by treating Lauth's violet with an alkali. In the latter case the imido-group is eliminated as ammonia.

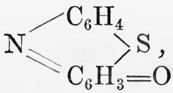
The base forms yellowish-brown leaflets, with a green reflex; the hydrochloride crystallises in fine black needles, forming a reddish-violet solution with water.

The dimethyl derivative of thionoline (Methylene Violet) is formed by boiling methylene blue with alkali, methylene azure, the sulphone of methylene blue, $C_{16}H_{17}N_3SO_2$, being simultaneously produced [36].

The base of dimethylthionoline, $C_{14}H_{12}SN_3O$, forms long needles, and its alcoholic solution shows a reddish-brown fluorescence.

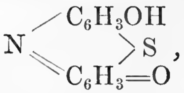
The hydrochloride crystallises in brilliant green needles which dissolve in concentrated sulphuric acid with a green colour, and dyes silk violet.

Oxythiodiphenylimide [36],



is produced by oxidation of oxythiodiphenylamine (from oxydiphenylamine and sulphur). It forms reddish-brown needles which dissolve sparingly in ether, acetone, &c., with an orange-red colour.

Thionol (*Dioxythiodiphenylimide*) [36],



is formed, along with thionoline, by boiling Lauth's violet with alkali or dilute sulphuric acid, and also by treating thiodiphenylamine with sulphuric acid containing 75 per cent. SO_3. It is insoluble in water and crystallises from hydrochloric acid in needles, which contain hydrochloric acid. It possesses simultaneously weak basic and strong acid properties.

The acid solutions are reddish violet, the alkaline solutions violet in colour.

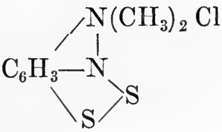
The barium salt, $C_{12}H_7NSO_2BaO$, forms brilliant green leaflets soluble in water.

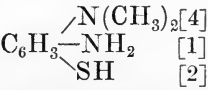
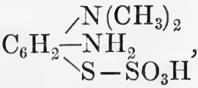
Methylene Red [19, 36, 53].

$C_8H_9N_2S_2$.

This compound is a bye-product in the preparation of methylene blue by the old process. Its formation is greatest in presence of a large amount of sulphuretted hydrogen.

Its constitution is expressed by the formula



This is deduced from the following properties. On reduction it yields dimethylparaphenylenediamine-mercaptan 
$C_6H_3\begin{cases} N(CH_3)_2 & [4] \\ NH_2 & [1] \\ SH & [2] \end{cases}$
and is decolorised by alkalies, the corresponding thiosulphonic acid, 
$C_6H_2\begin{cases} N(CH_3)_2 \\ NH_2 \\ S-SO_3H \end{cases}$
, being formed amongst other compounds.

The hydrochloride, $C_8H_9N_2S_2,HCl$, is easily soluble in water, and is extracted from the solution by phenol. The hydriodide is more sparingly soluble and crystallises from water in thick prisms. On reduction, and subsequent oxidation with dimethylaniline, methylene blue is formed.

Methylene Green.

This compound is obtained by treating methylene blue with nitrous acid. It dyes textile fibres a fine dark green colour, and appears, from its properties, to be a nitro-derivative of methylene blue. In its behaviour towards fibres it resembles the latter.

4. OXYINDAMINES AND OXYINDOPHENOLS.

(OXAZINES.)

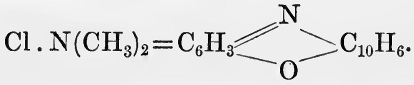
This denomination includes a series of compounds analogous to the thioindamines and containing an oxygen atom in place of the sulphur atom of the latter.

These compounds are formed by the action of nitrosodimethylaniline or of quinonedichlorimide on certain phenols or phenolcarbonic acids in a hot alcoholic or acetic acid solution, or by oxidation of these phenols with paradiamines at a medium temperature.

The dyestuffs from β-naphthol and from gallic acid are best known. The former was discovered almost simultaneously by Witt and Meldola.

Naphthol Blue [29, 51].

$C_{18}H_{15}N_2O . Cl$ =



This dyestuff is best prepared by heating nitrosodimethylaniline hydrochloride with β-naphthol in alcoholic solution. A part of the nitrosodimethylaniline becomes reduced to dimethylparaphenylenediamine during the reaction.

The base is soluble in benzene with a red colour.

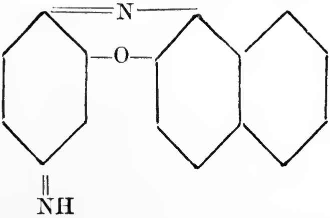
The hydrochloride, $C_{18}H_{14}N_2O,HCl$, and the zinc chloride double salt form bronzy needles, which form blue-violet solutions with water.

Platinum double salt, $(C_{18}H_{14}N_2O,HCl)_2PtCl_4$.

The compound dyes on cotton prepared with tannic acid, and produces a somewhat dull violet-blue shade similar to indigo. The dyestuff is known commercially as Fast Blue, Naphthol Blue, and

Meldola's Blue. The dyestuff exerts an extremely irritating action on the mucous membrane of the nostrils.

β-naphthol reacts with chlorquinonediimide, producing a red dyestuff of the composition $C_{16}H_{10}N_2O$ [51]. It does not form a diazo-compound, and therefore probably contains no free amido-group. Its constitution is probably expressed by the formula—



The base has a yellow colour without fluorescence, the salts dissolve in concentrated sulphuric acid with a green colour, which on dilution turns through blue to red.

Under similar conditions α-naphthol yields a dyestuff which dissolves in dilute hydrochloric acid with a red colour, and produces a greyish-violet shade in dyeing.

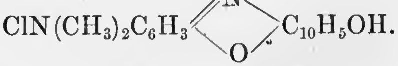
Resorcin reacts with nitrosodimethylaniline, producing a fluorescent violet dyestuff [29].

Sulphonic acids of this series may also be obtained from sulphonic acids of the phenols.

Muscarine.

$C_{18}H_{15}N_2O_2Cl.$

This dyestuff is an hydroxyl derivative of naphthol blue, and is obtained by interaction of nitrosodimethylaniline hydrochloride and a dioxynaphthalene, M.P. 186°. Its constitution is represented by the formula :—



$$ClN(CH_3)_2C_6H_3\langle{}^{N}_{O}\rangle C_{10}H_5OH.$$

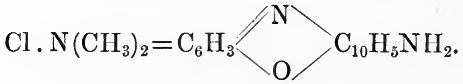
The base is yellowish brown, and is obtained by precipitating the violet solution of one of the salts with an alkali. It forms a bluish-green solution with concentrated sulphuric acid, and on dilution the colour changes through blue to violet, a violet precipitate being formed finally. It dyes a dull blue shade on cotton mordanted with tannic acid.

Nile Blue.

$(C_{18}H_{16}N_3O)_2SO_4$.

This dyestuff is prepared by heating α-naphthylamine hydrochloride with nitrosodimethylmetamidophenol hydrochloride in acetic-acid solution to 100°. Nile blue is soluble in water and alcohol with a blue colour. Alkalies produce a brownish precipitate, soluble in ether with a brown fluorescence. Sulphuric acid dissolves it with a yellow colour, which on dilution changes through green to blue. On adding hydrochloric acid to an aqueous solution of Nile blue, the sparingly soluble hydrochloride is precipitated.

The hydrochloride has the constitution expressed by the formula:



$$Cl\,.\,N(CH_3)_2{=}C_6H_3\begin{matrix}N\\O\end{matrix}C_{10}H_5NH_2.$$

Nile blue dyes on cotton prepared with tannic acid and tartar emetic, producing a greenish-blue shade of great beauty and purity, similar to methylene blue, but clearer.

Gallocyanine [32, 51].

This dyestuff has attained considerable importance, especially in calico-printing, and is obtained by acting with nitrosodimethylaniline hydrochloride on gallic acid in a hot alcoholic or acetic acid solution. The compound crystallises out in brilliant green needles. The mother-liquors always contain dimethylparaphenylenediamine.

Gallocyanine is sparingly soluble in hot water, alcohol, and acetic acid. The solutions have a violet colour. It possesses simultaneously acid and basic properties, and is precipitated from the reddish-violet alkaline solution by acids.

Gallocyanine dissolves with difficulty in hydrochloric acid, forming a reddish-violet solution. Its solution in strong sulphuric acid is blue.

It forms an almost colourless crystalline compound with sodium bisulphate.

The composition of gallocyanine is expressed by the formula—

$$C_{15}H_{12}N_2O_5\,;$$

and its formation is explained by the following equation :—

$$\underset{\substack{\text{Nitrosodimethyl-}\\\text{aniline.}}}{3C_8H_{10}N_2O} + \underset{\substack{\text{Gallic}\\\text{acid.}}}{2C_7H_6O_5} = \underset{\text{Gallocyanine.}}{2C_{15}H_{12}N_2O_5} + \underset{\substack{\text{Dimethyl-}\\\text{paraphenyl-}\\\text{diamine.}}}{C_8H_{12}N_2} + \underset{\text{Water.}}{H_2O.}$$

Gallocyanine is easily soluble in hot aniline, and, on cooling, an anilide crystallises in long green needles. This anilide is formed by action of two molecules of aniline, according to the equation—

$$C_{15}H_{12}N_2O_5 + 2C_6H_5NH_2 = C_{27}H_{24}N_4O_4 + H_2O.$$

This compound may be regarded as an aniline addition-product of the anilide—

$$C_{15}H_{12}N_2O_4{=}NC_6H_5 \quad [51].$$

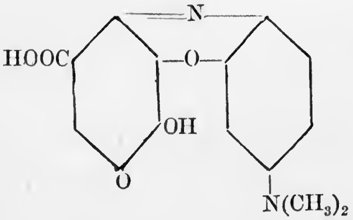
The anilide possesses well-marked basic properties.

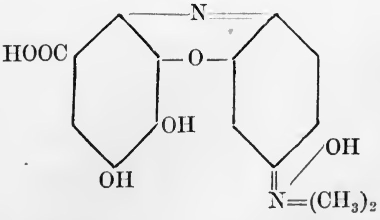
The methyl-ether of gallic acid reacts with nitrosodimethylaniline, producing a methyl-ether of gallocyanine, $C_{15}H_{11}N_2O_5(CH_3)$. This compound is a dyestuff, and is known in commerce as Prune [51].

Prune differs from gallocyanine inasmuch as the former is a base forming stable soluble salts, while in gallocyanine the acid properties are predominant.

Nitrosodimethylaniline reacts also with the amide of gallic acid ("gallaminic acid"), and forms a blue dyestuff, which is met with in commerce in form of its bisulphite compound under the name Gallamine Blue.

Gallocyanine is constituted according to one of the following formulæ :—





From the fact that the methyl-ether of gallocyanine yields a diacetyl derivative, the second formula appears the more probable. The pentatomic nitrogen present is probably saturated by the carboxyl group in gallocyanine, or by an hydroxyl group in Prune, as the base contains no ammonium hydroxyl group.

These three dyestuffs are capable of dyeing on mordants, and produce violet lakes with iron, aluminium, and especially with chromium oxides. On account of the fastness of the shades produced, these dyestuffs are largely used in calico-printing and in wool-dyeing. In printing, a mixture with sodium bisulphite and chromium acetate is used, the insoluble chromium-lake being produced by steaming. Wool may be dyed without any mordant, but faster shades are obtained by chroming the wool first. Prune having more pronounced basic properties may be dyed on cotton prepared with tannic acid and tartar emetic.

Prune comes into the market as a powder; Gallocyanine and Gallamine Blue generally as pastes.

5. DICHROÏNES.

Liebermann's Phenol Dyestuffs [30].

As it has been demonstrated that certain of these dyestuffs are derivatives of phenoxazine, they are best described here.

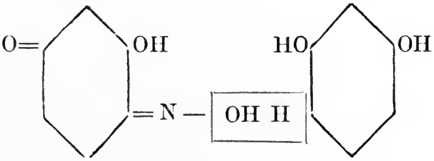
On treating phenols in concentrated sulphuric acid solution at 40°–50° C. with nitrous acid, peculiar violet or blue compounds are formed. They are of distinctly acid character, and are reprecipitated from alkaline solutions on addition of acids. Their alkaline solutions exhibit a remarkable fluorescence, and for this reason this class of compounds is also known as Dichroïnes.

The dyestuff from phenol has the composition, $C_{18}H_{15}NO_3$. It forms a brown powder, insoluble in water, soluble in alkalies with a blue colour. The thymol dyestuff has the formula $C_{30}H_{36}N_2O_4$, and the orcin dyestuff $C_{21}H_{18}N_2O_6$. Both have a violet colour.

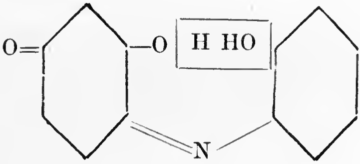
Resorufin (*Weselsky's Diazoresorufin*).

$C_{12}H_7NO_3$. [31, 33, 34, 54.]

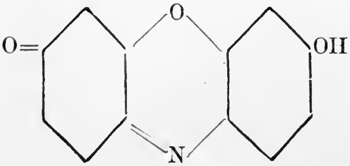
This compound is formed by action of nitro- or nitrosoresorcin or nitrobenzene on resorcin in presence of concentrated sulphuric acid at 170°. It may also be obtained from resazurin (see below) by various methods. Resazurin yields resorufin on heating alone or with concentrated sulphuric acid to 110°, by reduction with sodium bisulphite, or with zinc powder or iron, and subsequent oxidation in the air. Resorufin is also formed in the preparation of resazurin. The following synthetic methods give a clear idea of its constitution. On dissolving an equal number of molecules of nitrosoresorcin and resorcin in concentrated sulphuric acid a dyestuff is formed, which, on heating the mixture to 100°, goes over into resorufin. The intermediate product of the reaction may be regarded as an indophenol of resorcin formed according to the scheme :—



On heating to 100°, another molecule cf water is eliminated, thus :—



and the resulting resorufin has accordingly the constitution expressed by the formula—

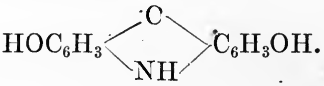


Resorufin is also formed by heating nitrosophenol or quinonechlorimide with resorcin, or by heating nitrosoresorcin with phenol or by oxidation of paramidophenol with resorcin, or by oxidation of asymmetrical amidoresorcin with phenol. These reactions are all carried out in presence of concentrated sulphuric acid.

Resorufin forms small brown needles, insoluble in water, sparingly soluble in alcohol and ether, and easily soluble in hot concentrated hydrochloric acid. It dissolves readily in alkalies, and the solution exhibits a beautiful cinnabar-red fluorescence.

Resorufin ethyl-ether, $C_{12}H_6NO_3(C_2H_5)$, is formed by heating the silver salt with ethyl iodide and alcohol. It forms orange-red needles, M.P. 225°.

Hydroresorufin (*Dioxyphenoxazin*) :—



$$HOC_6H_3{<}\genfrac{}{}{0pt}{}{O}{NH}{>}C_6H_3OH.$$

This is a leuco-compound formed by reduction of resorufin in acid solution. It forms long silky needles, M.P. 216°. In alkaline solution it oxidises rapidly to resorufin.

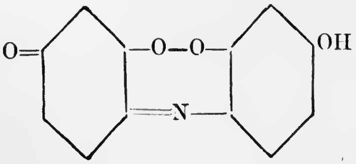
Tetrabromresorufin is obtained by action of bromine on an alkaline solution of resorufin. Its sodium salt, $C_{12}H_2Br_4NO_3Na + 2H_2O$, forms the commercial Resorcin Blue or Fluorescent Blue. It dyes wool and silk in an acid bath, and produces bluish-violet shades, remarkable for their beautiful red fluorescence.

Resazurin (*Weselsky's Diazoresorcin*). [31, 33, 34.]

$C_{12}H_7NO_4$.

This compound is formed by action of nitrous acid on an ethereal solution of resorcin. It forms lustrous green prisms, which are insoluble in water and ether, sparingly soluble in alcohol, and easily soluble in alkalies. The alkaline solutions are violet, and have a brown fluorescence.

The constitution of resazurin is not known with certainty. It contains one oxygen atom more than resorufin, and the two are evidently closely related from the ease with which resazurin may be transformed into resorufin. The two also yield the same dioxyphenazoxin on reduction. It is probable that resazurin is expressed by the formula :—



Acetyl resazurin, $C_{12}H_6NO_4(C_2H_3O)$, forms long red needles, M.P. 222°.

Resazurin ethyl ether, $C_{12}H_6NO_4(C_2H_5)$, forms dark red needles, M.P. 215°.

Orcirufin. [33, 34, 55.]

$C_{14}H_{11}NO_3$.

This compound is formed by action of nitrous acid on an ethereal orcin solution, and is identical with the dyestuff obtained by Liebermann by action of nitrous acid on orcin in presence of sulphuric acid.

Orcirufin yields a monoacetyl derivative, M.P. 204°.

Resorufamin, $C_{12}H_8N_2O_2$.—This body is closely related to resorufin, one oxygen atom of the latter being replaced by an amido-group. It is obtained by heating quinonedichlorimide with resorcin in alcoholic solution.

Resorufamin is only obtained in small quantity. It is a base forming salts which are easily soluble, and the solutions exhibit practically the same fluorescence as the alkaline solution of resorufin.

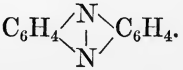
Orcirufamin, $C_{13}H_{10}N_2O_2$, is obtained in a similar manner, but is formed in larger quantity. It closely resembles the above.

Lacmoïd.—This colouring-matter, which probably belongs to the above series, was obtained by heating resorcin with sodium nitrite [46, Traube and Hock]. It forms blue salts with alkalies, and their solutions are turned red by acids. For this reason it has been proposed as an indicator in titration.

CHAPTER VII.

AZINE DYESTUFFS.

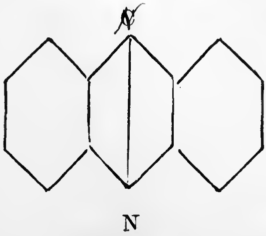
THIS chapter comprises the saffranines and their allies, amongst which are the eurhodines, toluylene red, the so-called neutral dyes, Basle blue, and probably Magdala red and Mauveine. Most of these dyestuffs have been long known, but we owe most of our knowledge of their constitution to the researches of Witt on the eurhodines. Witt observed that a compound of this class [37], obtained by action of *a*-naphthylamine on ortho-amidoazotoluene, gives, on removal of the amido-group, tolunaphthazine (naphthylene-toluylenequinoxaline). All these dyestuffs are derivatives of an azine (quinoxaline of Hinsberg). The simplest body of the azine group is phenazine (azophenylene of Claus and Rasenack) :—



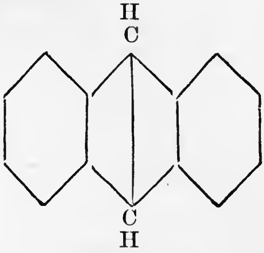
$$C_6H_4\left\langle\begin{matrix} N \\ | \\ N \end{matrix}\right\rangle C_6H_4.$$

The group  $\left\langle\begin{matrix} N \\ | \\ N \end{matrix}\right\rangle$, which replaces two ortho-hydrogen atoms in each benzene ring, is the chromophor of the whole series.

The azine group, with the four adjacent carbon atoms, forms a new ring, containing six atoms, so that phenazine may be regarded as containing three rings, like anthracene.



Phenazine.

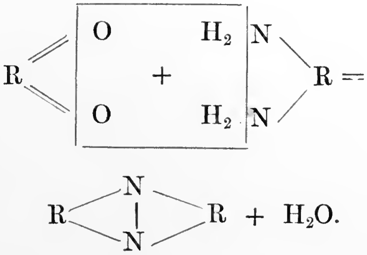


Anthracene.

The azines are in some respects analogous to the quinone-anilides.

While in the reaction between a paraquinone and a diamine, only one amido-group enters into the reaction with one quinone group, the action of an orthodiamine and an orthoquinone is just double, both oxygen atoms being eliminated in form of water with the hydrogen of the amido-group, the nitrogen of the latter entering in the place of the oxygen.

The reaction will be easily understood from the following graphic equation:—



The simplest azines are not dyestuffs, they are slightly coloured bodies, generally yellow, and possessing weak basic properties, their salts being decomposed by water.

The introduction of amido-groups intensifies the basic character of the azine, and increases the dyeing properties.

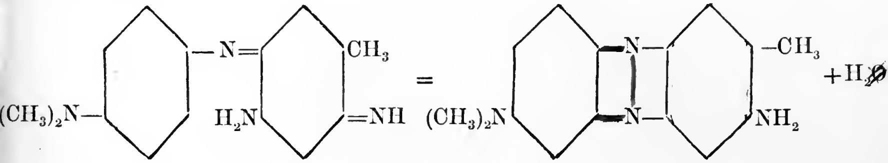
Hydroxyl groups produce colouring-matters of a slightly acid nature, which have, however, only little tinctorial power.

Monamidoazines (Eurhodines) are only weak dyestuffs, the dyeing-power being fully developed by introduction of two or more amido-groups.

The azines are closely related to the indamines; the latter being derivatives of paraquinonediimide, while the former correspond to the orthoquinonediimides, only in this case the condensation so common in the ortho series takes place.

The relationship between the two classes of compounds is shown by the fact that the indamines may be easily converted into azines, and that monamines, with a free para position capable of yielding indamines on oxidation, give azines when the para positions are occupied. The conversion of indamines into azines is especially instructive in the case of amidoindamines—for example, Toluylene blue. On heating an aqueous solution of this compound for some time, Toluylene red, an amidoazine, is formed with elimination of hydrogen. The hydrogen is not liberated as such, but converts a portion of the toluylene blue to its leuco-base [4].

The reaction will be readily understood from the following equation:—



Toluylene blue. Toluylene red.

The amido-group adjacent to the nitrogen atom linking the benzene chains in the indamine, loses its hydrogen atoms, and becomes linked to the second benzene chain, while the imido-group is simultaneously reduced to an amido-group.

If an oxidising agent is present, the conversion of toluylene blue into leuco-base does not take place.

The simpler indamines only yield azines in presence of a primary amine. In this case saffranines are formed. These bodies contain probably a phenylazonium group, viz., an azine group containing a pentatomic nitrogen atom, which is linked with chlorine and a benzene ring.

Although the basic character of the azines is increased by the introduction of amido-groups, the azine group plays the principal part in the formation of salts. If acetyl groups are introduced into the amido-groups the basic properties of the compound are decreased, but not entirely destroyed.

A further confirmation of this is seen in the behaviour of the polyacid salts and of the corresponding diazo-compounds.

Diamidoazines generally form three series of salts, of which the monoacid are red, the diacid blue, and the triacid green. The two latter compounds are decomposed by water, the first one is stable.

If a diazo-group is introduced into a diamidoazine the compound forms stable diacid salts, which have likewise a blue colour. With a second diazo-group a stable green salt may be obtained.

As diazo-groups can only be formed from amido-groups, and as the conversion into diazo-compound increases the stable salt-forming capacity once for each diazo-group, it is a necessary conclusion that the acid radical present in the red stable salt cannot be connected with the amido-groups.

Another point in this connection is that the amidoazines dye fibres the colour of the monoacid, and not of the polyacid salts, thus showing that the azine group effects the combination with the fibre.

In the monamidoazines both nitrogen atoms appear capable of combining with acids, at least this is probable from the various colour-reactions which these bodies give with strong acids.

The azine dyestuffs mostly possess a well-marked fluorescence; this appears in some cases in the alcoholic solutions of the salts, and in others in the ethereal solution of the base.

1. EURHODINES [37, 38].

(AMIDOAZINES.)

This class of bodies was discovered by Witt. They are formed by action of orthoamidoazo-compounds on monamines (orthoamidoazotoluene on α-naphthylamine), by action of orthoquinones on triamines with two adjacent amido-groups, and by action of nitrosodimethylaniline or of quinonedichlordiimide on certain monamines, in which the para position is occupied [50, 52].

The eurhodines are in general weak basic dyestuffs. The base is usually yellow, the monoacid salts red, and the diacid salts green. Both are readily decomposed by water. The monoacid salts dye silk red, but on washing a change to the yellow colour of the base takes place. Most eurhodines give a red solution with concentrated sulphuric acid, the colour changing through black and green into red again on dilution. The ethereal solutions of the bases exhibit a yellowish-green fluorescence.

Eurhodine,

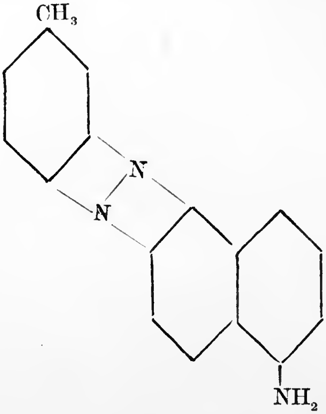
$C_{17}H_{13}N_3$ [37].

(*Amidotolunaphthazine.*)

This compound is obtained by heating orthoamidoazotoluene with α-naphthylamine hydrochloride. The base forms golden-yellow needles sparingly soluble in alcohol and ether, easily in aniline and phenol. It sublimes without decomposition. The ethereal solution shows a green fluorescence. Concentrated sulphuric acid dissolves it with a red colour, which changes through black and green into red on dilution. It reacts with nitrous acid producing a diazo-compound, which is decomposed on boiling with alcohol, eurhodol ethyl ether, $C_{17}H_{11}N_2-O-C_2H_5$, being formed.

The hydrochloride, $C_{17}H_{13}N_3,HCl$, forms deep red, bronzy needles.

Witt accords the following constitution to this eurhodine [28]:

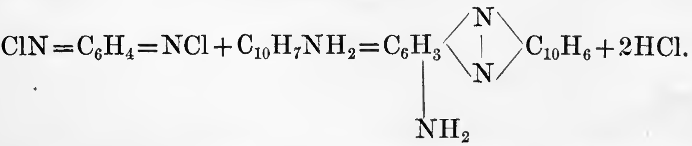


Eurhodine,

$$H_2N-C_6H_3\left<\begin{matrix}N\\|\\N\end{matrix}\right>C_{10}H_6$$ [50].

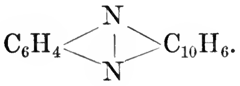
(*Amidophennaphthazine.*)

Is formed by action of quinonedichlordiimide on β-naphthylamine according to the following equation:—

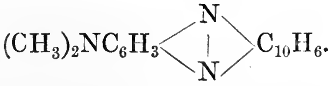


$$ClN=C_6H_4=NCl+C_{10}H_7NH_2=\underset{\displaystyle NH_2}{\underset{|}{C_6H_3}}\left<\begin{matrix}N\\|\\N\end{matrix}\right>C_{10}H_6+2HCl.$$

The base has a yellow colour, and fluoresces in ethereal solution. The salts are red, without fluorescence, and are decomposed by water. The compound forms a brown solution with concentrated sulphuric acid. It yields naphthophenazine on boiling with nitrous acid and alcohol:—



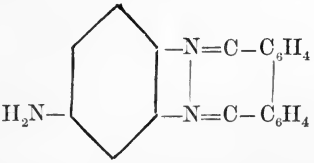
Dimethylamidophennaphthazine,



is prepared by action of nitrosodimethylaniline on β-naphthylaniline [52].

The base is yellow, dissolves in concentrated sulphuric acid with a violet colour, and forms blue unstable salts [52].

Amidophenophenanthrazine.



This eurhodine is formed by action of phenanthrenequinone on unsymmetrical triamidobenzene. The base forms yellow flocks or a brown crystalline powder. The salts are sparingly soluble, and of a carmine-red colour. The reactions are similar to those of the preceding compounds [38].

Eurhodines are also formed by the action of triamidobenzene on β-naphthoquinone, glyoxal, benzil, isatine, and leuconic acid.

A dimethyl eurhodine (dimethylamidophenotoluazine),

$$(CH_3)_2N-C_6H_3=N_2=C_6H_3CH_3 \text{ [39]},$$

is formed on boiling diazotised toluylene red with alcohol.

2. EURHODOLS.

(OXYAZINES.)

These bodies are formed by melting the azinesulphonic acids with caustic potash [40] and by heating the eurhodines with concentrated hydrochloric acid to 180° [38].

They resemble the eurhodines in colour and fluorescence, and in their reactions with concentrated sulphuric acid, but differ in possessing both phenolic and basic properties.

Oxynaphthotoluazine,

$C_{17}H_{12}N_2O$.

This eurhodol is obtained by heating the corresponding eurhodine, $C_{17}H_{13}N_3$, with hydrochloric acid or dilute sulphuric acid. It dissolves in concentrated sulphuric acid with a red colour, and is precipitated from this solution in yellow flocks on addition of water [38].

Eurhodol,

$C_{24}H_{14}N_2O$.

(*Oxyphenanthrenenaphthazine.*)

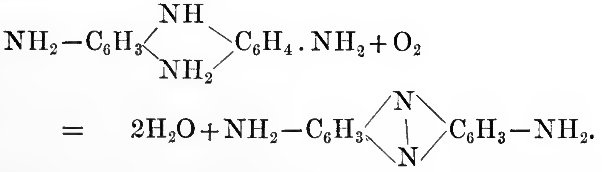
This compound is formed by melting phenanthrene-naphthazine-sulphonic acid (from phenanthrenequinone and $\alpha\beta$-naphthylenediaminesulphonic acid) with caustic potash. It dissolves in concentrated sulphuric acid with a blue colour, which suddenly changes into bright red on dilution. Its sulphonic acid is a yellow dyestuff.

The colour-reactions exhibited by the eurhodols with acids of different concentrations can only be explained on the assumption that mono- and diacid salts exist, in which, according to circumstances, one or both nitrogen atoms of the azine group exert basic functions.

3. TOLUYLENE RED.

$$(CH_3)_2NC_6H_3\left\langle\begin{array}{c}N\\|\\N\end{array}\right\rangle C_6H_2\left\langle\begin{array}{l}CH_3\\NH_2\end{array}\right. \quad [4].$$

Toluylene Red is a diamidoazine, the simplest of which, diamidophenazine, is obtained by oxidation of triamidophenylamine with manganese dioxide.



$$NH_2-C_6H_3\left\langle\begin{matrix}NH\\NH_2\end{matrix}\right\rangle C_6H_4.NH_2+O_2$$

$$= \quad 2H_2O+NH_2-C_6H_3\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_6H_3-NH_2.$$

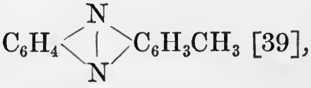
Toluylene red is a dimethyl derivative of a homologue of diamidophenazine, and is prepared by oxidation of dimethylparaphenylenediamine with metatoluylenediamine at the boil, and is also formed by heating toluylene blue (amidoindamine) [4] (see introduction to the Azine Dyestuffs). The base forms orange-red crystals, which contain four molecules of water. The water may be expelled at 150°, leaving the anhydrous compound, which is of a blood-red colour [4]. The alcoholic and ethereal solutions fluoresce strongly.

The monoacid hydrochloride is a fine red dyestuff, which is turned blue by hydrochloric acid, and green by concentrated sulphuric acid. The zinc-chloride double salt forms crystals with a metallic lustre [4].

Toluylene red comes into commerce as Neutral Red, and being a basic dyestuff is fixed on cotton by means of tannic acid.

Toluylene red contains one free amido-group and yields a diazo-compound, which gives a dimethyl eurhodine on boiling with alcohol [39].

By oxidation of paraphenylene-diamine and metatoluylenediamine, a non-methylated toluylene blue is formed which yields a corresponding toluylene red on heating. This latter forms a tetrazo-compound which yields methylphenazine (benzenetolazine):



$$C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_6H_3CH_3 \ [39],$$

on boiling with alcohol.

A violet dyestuff, Toluylene Violet, to which Witt ascribes the formula $C_{14}H_{14}N_4$, is formed by treating toluylene blue with an excess of metatoluylenediamine [4]. A similar dyestuff, known commercially as Neutral Violet, is the product of the oxidation of dimethylparaphenylenediamine with metaphenylenediamine.

4. SAFFRANINES [1, 2, 3, 4].

The dyestuffs coming under this classification contain four nitrogen atoms. Unlike the previous azine dyestuffs, they contain at least three hydrocarbon chains. Although their behaviour shows them to be phenazine derivatives, they differ in many respects from those previously described. Especially noticeable is their strong basic character, which in many respects resembles that of the quaternary ammonium bases, and the characteristic bitter taste of the latter compounds is also present in the saffranines. Another point of difference from the rest of the azine dyestuffs is that the free base has the same colour as the mono-acid salts.

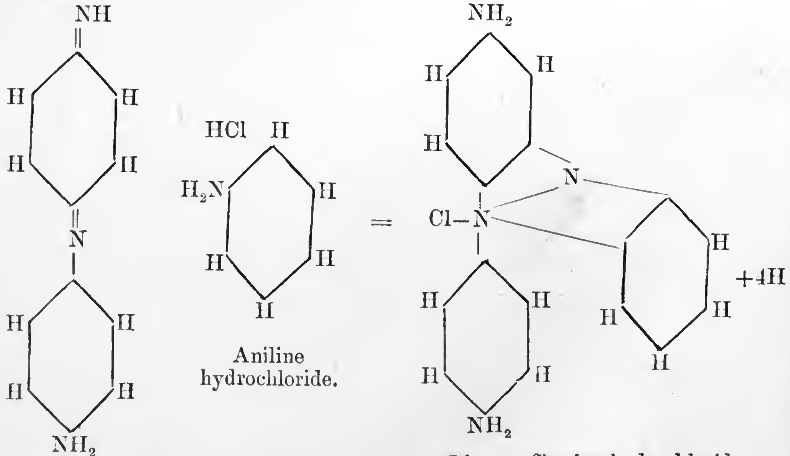
The well-marked basic properties of the saffranines are doubtless functions of the azine group, although two amido-groups are also present. The hydrogen atoms of the latter may be replaced by alcohol or acid radicals; and from the fact that the diacetyl derivatives are still mono-acid bases, it is evident that the strongly basic properties of the azine group remain unaffected.

The saffranines form three series of salts. The mono-acid salts are, like the base, red and very stable; the diacid salts are blue, and the triacid green. The two latter series are decomposed by water; and in fact the green salts can only exist in presence of concentrated sulphuric or hydrochloric acids. Both amido-groups may be diazotised [1]. The primary diazo-compound forms blue diacid salts, which are formed in slightly acid solutions, and correspond to the blue diacid saffranine salts. The green tetrazo-compounds have not been analysed, but probably correspond to the triacid salts. The salts of these diazo-compounds are not decomposed by water.

The saffranines are products of the following reactions:—By heating primary monamines with indamines, whereby part of the latter undergo reduction [1, 3, 4]; by oxidation of paradiamido-diphenylamine and its analogues with primary bases [1]; and by oxidation of paradiamines with two molecules of the latter [3, 4].

In the oxidation of paradiamines with monamines two different monamines may be used, of which one only need be primary. For the diamine and one monamine the same conditions must be observed as for the production of an indamine, *i. e.* that the diamine must only be substituted in one amido-group, and the monamine must possess a free para position. As an indamine is always formed as an intermediate product, all three processes may be said to depend on the same reaction—*i. e.* an indamine is formed either from diamidodiphenylamine or from the diamine and one molecule of monamine. The monamine used in the second stage of the process must not be substituted in the amido-group, but the para position need not be free. As, however, certain monamines are not capable of reacting in this sense, as, for example, ortho substituted monamines such as mesidine and adjacent metaxylidine do not form saffranine with indamines [41], it may be conjectured that the monamine not only becomes connected through its nitrogen atom, but also through an ortho position in the ring. This assumption receives further confirmation from the fact that the formula of the simplest saffranine cannot be symmetrical, as the amido-groups react differently. Two different dialkyl saffranines, each substituted in one amido-group, may be prepared, each yielding a diazo-compound, and therefore each containing one free amido-group.

Numerous formulæ have been proposed to express the constitution of the simplest saffranine in accordance with the above facts; that of Witt, however, alone fulfils the necessary conditions. According to Witt the formation of saffranine from the simplest indamine and aniline proceeds as shown in the following schematic equation :—

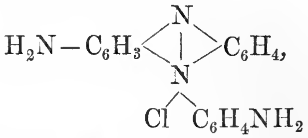


Indamine.

Aniline hydrochloride.

Phenosaffranine hydrochloride.

According to this assumption the aniline becomes connected with the nitrogen atom of the diphenylamine through its benzene ring, and a derivative of triphenylamine is formed, the indamine link being dissolved. The nitrogen atom of the aniline simultaneously enters one benzene chain of the indamine, in the ortho position to the diphenylamine nitrogen atom, and the nitrogen atoms become linked and form the azine ring. This saffranine formula may be shortly written thus :—



$$H_2N-C_6H_3\left\langle\begin{array}{c}N\\ |\\ N\end{array}\right\rangle C_6H_4,\qquad N\begin{cases}Cl\\ C_6H_4NH_2\end{cases}$$

and corresponds completely with the properties of the compound.

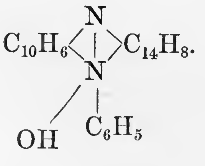
Here the amido-groups have different values, and this explains the isomerism of the alkyl-substitution products. The pentatomic nitrogen atom, simultaneously linked with chlorine and benzene, offers distinct reason for the stability of the monoacid saffranine salts.

Further evidence is afforded by the fact that the saffranine base contains one molecule of water, and that other phenylazonium compounds have been prepared synthetically.

Witt obtained such a compound by action of phenanthrenequinone on orthoamidophenyl-β-naphthylamine,

$$H_2N—C_{10}H_6—NH—C_6H_5,$$

and ascribes the following formula to it :—



$$C_{10}H_6\left\langle\begin{array}{c}N\\ |\\ N\end{array}\right\rangle C_{14}H_8.\qquad N\begin{cases}OH\\ C_6H_5\end{cases}$$

The dyestuffs obtained by action of nitrosodimethylaniline or of quinonedichlorimide on phenyl-β-naphthylamine are also probably members of this class of compounds [50, 52].

The monoacid salts of the saffranine series are generally red; the introduction of alcohol radicals into the amido-groups makes the shade more violet, while the introduction of methoxyl and ethoxyl groups into the benzene ring tends to produce yellower shades.

The saffranines are dyed on cotton mordanted with tannic acid, and produce the shade of their monoacid salts. Unmordanted cotton is capable of fixing small amounts of saffranine.

The diacid salts are produced by concentrated hydrochloric acid and are blue; the green triacid salts are obtained with concentrated sulphuric acid. Both are only capable of existence in presence of excess of acid, and are decomposed by water with formation of a monoacid salt. The bases may be obtained by decomposition of the sulphates with barium hydrate; they are of the same colour as the monoacid salts, and are easily soluble in water. They form carbonates with carbonic acid.

The saffranines yield leuco-compounds on reduction, which are pretty stable in acid solution, but are almost immediately oxidised to the original dyestuff in presence of alkalies. If the reduction be effected with acid stannous-chloride solution, one molecule of saffranine is found to require one molecule of stannous chloride, showing that two atoms of hydrogen are required for the conversion of saffranine into its leuco-base.

Phenosaffranine, by continued boiling with zinc powder and hydrochloric acid, may be converted into a very stable colourless base, $C_{18}H_{19}N_3O$.

Besides the reactions already mentioned, saffranines are also formed by action of amines on amidoazo-compounds [45], by oxidation of the latter, and by oxidation of the mauveines [28]. The formation from amidoazo-compounds comes under one of the general methods, as it doubtless depends on the splitting up of the azo-compound into a paradiamine and a monamine.

The manufacture of the saffranines is always effected by the process which depends on the oxidation of one molecule of a paradiamine with two molecules of a monamine. The bases necessary are obtained by reduction of amidoazo-compounds. Orthotoluidine ("Echappés," the recovered oil from Magenta-manufacture, consisting of orthotoluidine and aniline, may be used) is submitted to the action of sodium nitrite and hydrochloric acid, whereby a mixture of amidoazotoluene and orthotoluidine is obtained; or, if Echappés are used, a mixture of amidoazotoluene, amidoazotoluenebenzene, amidoazobenzene, aniline, and orthotoluidine is produced. The mixture is then reduced with zinc or iron and hydrochloric acid, the result in the simplest case being the production of a mixture of one molecule paratoluylenediamine and two molecules of orthotoluidine, while the principal products from the mixture of bases are toluylenediamine and paraphenylenediamine with orthotoluidine and aniline. In any case the mixture is treated in dilute neutral solution with potassium bichromate and boiled, or the oxidation may be effected by manganese oxide

(Weldon mud) in presence of an organic acid. The first product is an indamine which yields a saffranine on further oxidation with the monamine. Violet dyestuffs are formed along with the saffranine, and these, being less basic, may be separated by soda and chalk, and the saffranine remaining in solution is salted out. The tolusaffranines are the only ones of importance, and their chief use is in cotton-dyeing. In conjunction with yellow dyestuffs (chrysoïdine, auramine, turmeric) they produce shades similar to Turkey red, but of course inferior as regards fastness. The saffranines are also used in silk-dyeing and produce beautiful rose shades.

Phenosaffranine [22, 1, 2, 3].

$C_{18}H_{14}N_4$.

This compound was first obtained by Witt by the oxidation of one molecule of paraphenylenediamine with two molecules of aniline [4]. It may also be obtained by oxidation of equal molecules of aniline and paradiamidodiphenylamine [1].

The free base may be obtained by decomposing the sulphate with an exactly equivalent quantity of barium hydrate. On evaporating the resulting solution *in vacuo*, the base suddenly crystallises out in green leaflets, and is then found to have lost its easy solubility in water.

The composition of the base dried at 100° corresponds to the formula

$$C_{18}H_{16}N_4O = C_{18}H_{14}N_4 + H_2O.$$

At 150° it loses about $\frac{1}{2}$ molecule of water.

Saffranine base is not very stable; it loses ammonia on boiling with water.

The alcoholic solutions of the base and its salts fluoresce strongly, while this property is entirely absent in aqueous solutions.

The *hydrochloride*, $C_{18}H_{14}N_4,HCl$, crystallises from dilute hydrochloric acid in brilliant green leaflets, and from water in long steel-blue needles. Its solution has a fine red colour. It is precipitated from its solutions by salt and by strong hydrochloric acid.

Nitrate, $C_{18}H_{14}N_4HNO_3$, forms green crystals sparingly soluble in water, and almost insoluble in dilute nitric acid [1, 2].

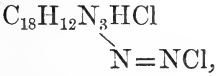
The *sulphate*, $C_{18}H_{14}N_4H_2SO_4$, forms steel-blue needles.

Platinum double salt [1], $(C_{18}H_{14}N_4HCl)_2\,PtCl_4$, forms lustrous golden leaflets, insoluble in water.

Diacetyl-hydrochloride [1], $(C_{18}H_{12}N_4)(C_2H_3O)_2HCl$, is obtained by the action of acetic anhydride and sodium acetate on phenosaffranine hydrochloride. It forms lustrous brown leaflets, and dissolves in alcoholic potash with a violet colour. It is decomposed on boiling with dilute sulphuric acid, acetic acid and phenosaffranine being produced.

Diazo-compounds [1].

The *diazochloride*,

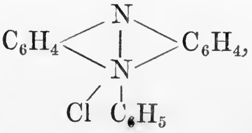


$$\begin{array}{l} C_{18}H_{12}N_3HCl \\ \qquad\qquad\;\;\diagdown \\ \qquad\qquad\quad N{=}NCl, \end{array}$$

is formed by action of nitrous acid on the (blue) acid solution of phenosaffranine hydrochloride. The solution of the compound is blue like the diacid saffranine salts, but unlike these does not change colour on dilution. Its *platinum double salt* forms broad blue needles.

The *gold salt*, $C_{18}H_{13}N_5Cl_2(AuCl_3)_2$, forms greenish-grey needles. On boiling with water two molecules of nitrogen are evolved. On boiling the diazo-compound with alcohol the base $C_{18}H_{13}N_3$ is formed (see below).

A tetrazo-compound of saffranine may be obtained in solution by treating the green solution of phenosaffranine in concentrated sulphuric acid with nitrous acid [1]. The colour of the solution is not changed on dilution. On boiling with alcohol a violet base, forming yellow salts, is produced. The chloride of this compound is probably phenazinephenyl-chloride,



the mother substance of the saffranines [43]. It is interesting to note that the colour-reactions of this compound with acids are exactly the same as those of the acetylated saffranines, from which it appears that the acetylation has the same effect as the removal of the amido-groups [43]. The compound in question is more easily obtained from the base $C_{18}H_{13}N_3$, the intermediate product in this case being a yellow diazo-compound.

α-Dimethylphenosaffranine [2],

$C_{18}H_{12}N_4(CH_3)_2$,

is formed by oxidation of one molecule of dimethylparaphenylenediamine with two molecules of aniline.

The *hydrochloride,* $C_{20}H_{18}N_4$,HCl, is a magenta-red dyestuff known commercially as Fuchsia.

The *nitrate,* $C_{20}H_{18}N_4,HNO_3$, forms lustrous green needles.

Platinum double salt, $(C_{20}H_{18}N_4HCl)_2PtCl_4$.

β-Dimethylphenosaffranine [41, 43].

This compound, isomeric with the above, is obtained by oxidation of one molecule of paraphenylenediamine with one molecule of dimethylaniline and one molecule of aniline. Its nitrate forms brown leaflets. For the crystallographic comparison of the nitrates see [43].

Tetramethylphenosaffranine [2].

$C_{18}H_{10}N_4(CH_3)_4$.

This dyestuff is formed by oxidation of one molecule of dimethylparaphenylenediamine, one molecule of dimethylaniline, with one molecule of aniline.

Hydrochloride, $C_{22}H_{22}N_4$,HCl.

Nitrate, $C_{22}H_{22}N_4,HNO_3$, is a fluorescent dyestuff forming brownish-violet thick crystals.

Diethylsaffranines [1].

$C_{18}H_{12}N_4(C_2H_5)_2$.

a. From one molecule of diethylparaphenylenediamine and two molecules of aniline, and

β. From equal molecules of paraphenylenediamine, diethylaniline, and aniline.

The hydrochlorides of both modifications form brilliant green needles, which are violet-red dyestuffs.

The *β*-hydrochloride is much more soluble in water than the *a*-compound.

Platinum salt, $(C_{22}H_{23}N_4Cl)_2PtCl_4$.

Acetyl derivatives [1].—Both diethylsaffranines yield basic monoacetyl derivatives on heating with acetic anhydride and sodium acetate. The hydrochlorides possess the formula

$$C_{22}H_{23}N_4Cl,C_2H_3O,$$

and form lustrous brown needles, soluble in water and alcohol with a violet colour. The alcoholic solutions do not fluoresce.

Diazo-compounds.

When treated with nitrous acid the diethylsaffranines yield diazo-compounds, analogous to the primary diazo-compounds of phenosaffranine. The solutions have a greenish-blue colour.

The chloride corresponds to the formula

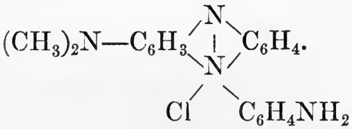
$$C_{22}H_{20}N_3HCl-N=NCl.$$

Platinum salt, $C_{22}H_{21}N_5Cl_2PtCl_4$, forms almost black needles with a coppery lustre.

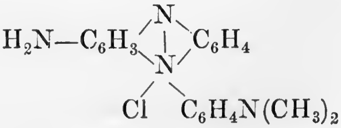
The fact that both modifications of dimethyl- and diethylsaffranine yield diazo-compounds, gives a certain proof of the presence of two amido-groups in saffranine.

Two isomeric monoethylsaffranines may be obtained in an analogous manner.

The constitution of the α- and β-compounds is probably expressed by the formulæ



α-Dimethylsaffranine.



β-Dimethylsaffranine.

(Compare Indamines.)

Tetraethylphenosaffranine [1],

$C_{18}H_{10}N_4(C_2H_5)_4$,

is obtained by oxidation of equal molecules of diethylparaphenylenediamine, diethylaniline, and aniline. It forms a zinc chloride double salt which forms beautiful crystals with a golden-yellow lustre. It is a bluish-violet dyestuff and exhibits a magnificent fluorescence on silk, but is speedily altered on exposure to light. It is known in commerce as Amethyst-Violet.

Platinum double salt, $(C_{26}H_{30}N_4,HCl)_2PtCl_4$.

Tetraethylsaffranine does not react with either nitrous acid or acetic anhydride.

Two dyestuffs, the constitution of which has not been definitely ascertained, but which from their method of preparation belong to the saffranine series, are Rubramine and Giroflé.

Rubramine is prepared by acting on orthotoluidine with nitrosodimethylaniline in hydrochloric acid solution. It comes into commerce as greenish-brown powder, and produces a fine red-violet shade on cotton mordanted with tannic acid.

Giroflé, probably a homologue of α-dimethylsaffranine (Fuchsia), is obtained by acting on xylidine with nitrosodimethylaniline. It is used for shading alizarine violet and reds.

Tolusaffranine [24].

$C_{21}H_{20}N_4$.

Hydrochloride, $C_{21}H_{20}N_4,HCl$, forms fine reddish-brown needles soluble in water and alcohol.

Platinum double salt, $(C_{21}H_{20}N_4HCl)_2PtCl_4$, forms a yellowish-red crystalline powder.

The *nitrate,* $C_{21}H_{20}N_4,HNO_3$, forms reddish-brown needles sparingly soluble in cold water.

Picrate, $C_{21}H_{20}N_4C_6H_2(NO_2)_3,OH$, forms reddish-brown needles insoluble in water and alcohol.

Besides the ortho-compound, formed by oxidation of one molecule of paratoluylenediamine, there exists a second one which is formed from equal molecules of toluylenediamine, aniline, and orthotoluidine, and is distinguished from the former by its lesser solubility. Both come into commerce as hydrochlorides. The latter, if prepared as usual from a mixture of aniline and toluidine, generally contains a lower homologue, $C_{20}H_{18}N_4$. These dyestuffs differ but little in shade, and produce on silk, wool, and cotton prepared with tannic acid, tones about halfway between magenta and ponceau. Dyestuffs which are to be regarded as oxymethyl- and oxyethyl-derivatives of phenosaffranine are produced by oxidation of paraphenylenediamine with two molecules of orthoanisidine or two molecules of orthoamidophenetol.

The orthoanisidine compound has probably the composition:—

$$C_{18}H_{12}(OCH_3)_2N_4.$$

Similar bodies are formed if the orthoanisidine is partly replaced by paranisidine or another primary monamine. These dyestuffs are especially characterized by their pure yellow shade. When dyed on silk they fluoresce strongly, the shades obtained resembling those produced by some of the eosines. Owing to their high price, however, they have not been used on a large scale.

The *compound* $C_{18}H_{13}N_3$ [43, 49] has already been mentioned as the product obtained on boiling the primary diazo-compound of phenosaffranine with alcohol. Its salts have a magenta-red colour and do not fluoresce in alcoholic solution. Concentrated sulphuric acid dissolves them with a yellowish-green colour, and on dilution the colour changes through green to red; the blue phase does not occur.

Nitrate, $C_{18}H_{13}N_3,HNO_3$, forms brown, difficultly soluble needles.

Zinc chloride double salt forms lustrous brown needles.

Acetyl derivative, $C_{18}H_{12}N_3C_2H_3O$, is a violet compound forming yellow monoacid salts.

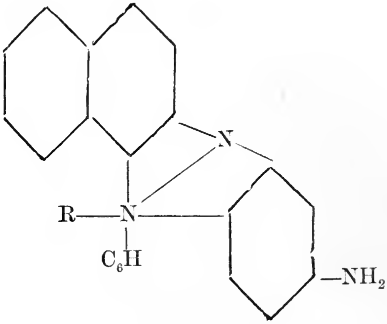
The compounds obtained by Witt [52], and by Nietzki and Otto [50, 51], by action of nitrosodimethylaniline and of quinonedichlorimide on phenyl-β-naphthylamine in all probability belong to this series.

By action of quinonedichlorimide on phenyl-β-naphthylamine, a violet base is produced forming magenta-red salts.

The compound dissolves in concentrated sulphuric acid with a violet colour which on dilution changes through dirty green into red. The composition of the salts may be expressed by the general formula $C_{22}H_{15}N_3 . R.$

Nitrate, $C_{22}H_{15}N_3,HNO_3$, forms fine needles or thicker lustrous green crystals.

The constitution of the compound is probably expressed by the formula [50] :—



The product of the interaction of nitrosodimethylaniline and phenyl-β-naphthylamine is a bluish-violet dyestuff, probably a dimethyl derivative of the former [52] : Neutral Blue.

Nitrosodimethylaniline reacts with paratoluyl-β-naphthylamine also, and produces a bluish-violet dyestuff of the composition

$$C_{25}H_{22}N_3Cl.$$

From the salts, a red base may be separated, which dissolves in alcohol with an orange-yellow fluorescence.

The compound dissolves in concentrated sulphuric acid with a red-violet colour, which on dilution changes through green and blue to violet. The nitrate is very sparingly soluble [52].

Saffranol.

$$C_{18}H_{12}N_2(OH)_2.$$

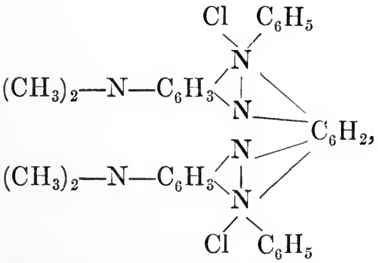
This compound is formed by continued boiling of phenosaffranine with baryta water, or alcoholic potash solution. It may be regarded as phenosaffranine in which both amido-groups are replaced by hydroxyl. The compound agrees with this assumption inasmuch as it possesses simultaneously acid and weak basic properties.

Saffranol forms brass-coloured leaflets, almost insoluble in indifferent solvents, but easily in ammonia and alkalies with a deep carmine-red colour. It is separated from these solutions by acids, and produces the sparingly soluble salts if an excess be present.

It forms a red diacetyl-compound, which yields yellow, sparingly soluble salts with acids [49].

Indazine M [53],

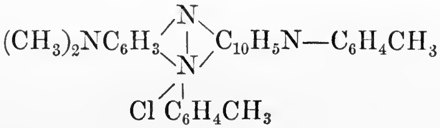
$C_{34}H_{30}N_6Cl_2 =$



is produced by action of nitrosodimethylaniline hydrochloride on diphenylmetaphenylenediamine. It dyes fine blue shades on cotton prepared with tannic acid.

Basle Blue [54].

$C_{32}H_{29}N_4Cl =$



This dyestuff is obtained by the action of nitrosodimethylaniline chlorhydrate on the ditolylnaphthylenediamine obtained by heating *a*-dioxynaphthalene (M.P. 180°) with paratoluidine and paratoluidine hydrochloride. The dyestuff forms a brownish crystalline powder, soluble in water with a bluish-violet colour. It dissolves in concentrated sulphuric acid with a greenish-blue colour, which on dilution changes through green to violet, a bluish-violet precipitate being formed. Basle blue is a basic dyestuff and is best dyed on cotton prepared with tannic acid and tartar emetic.

Azine Green [55]

is analogous to the above in constitution, and results from the action of nitrosodimethylaniline hydrochloride on the diphenylnaphthylenediamine obtained from dioxynaphthylene, M.P. 216°. It is a basic dyestuff, producing dark green shades which are pretty fast.

5. MAGDALA RED.

This dyestuff has been long known, and was investigated almost twenty years ago by Hofmann [27]; but from the recent researches of Julius [44] it appears that the earlier formula, $C_{30}H_{21}N_3$, is incorrect, and that its composition is analogous to that of the saffranines, its formula being $C_{30}H_{20}N_4$. Accordingly Magdala red may be regarded as a saffranine of the naphthalene series. Indeed the great stability of the dyestuff, its properties, and the strong fluorescence of its salts are strong arguments in favour of this assumption.

Magdala red is obtained by heating α-amidoazonaphthalene with α-naphthylamine hydrochloride in glacial acetic acid solution. The yield is extremely small. A better yield is claimed in a more recent modification of the above process, in which a mixture of the hydrochlorides of α-naphthylamine and paranaphthylenediamine is heated with amidoazonaphthalene to 130–140° till the melt has a pure red colour.

Analogous dyestuffs may also be obtained from mixtures of naphthylenediamine hydrochloride and amidoazobenzene, or with naphthylenediamineaniline and amidoazobenze [56].

Magdala red hydrochloride forms lustrous green needles, sparingly soluble in water, more easily in alcohol. The salt is not decomposed by ammonia or caustic soda [27]. The sulphate forms large green needles [45]. The picrate and platinum double salt are sparingly soluble in alcohol.

The alcoholic solutions of the salts exhibit a magnificent yellow fluorescence, which surpasses that of any of the saffranines. The salts dissolve in concentrated sulphuric acid with a bluish-black colour.

Magdala red still finds a slight application in special cases in silk-dyeing, but owing to its enormous price has been almost entirely superseded by rhodamine.

6. MAUVEINE [28].

$C_{27}H_{24}N_4$.

Mauveine was the first aniline dyestuff prepared on a large scale (Perkin, 1856), and is certainly closely related to the saffranine dyestuffs. Like these, it has strong basic properties, and gives similar reactions with sulphuric acid. Finally, a saffranine (para-saffranine, $C_{20}H_{18}N_4$ [28]) is formed by oxidation of mauveine in acetic acid solution. The fluorescence characteristic of alcoholic saffranine solution is, however, absent with mauveine.

Free mauveine forms a black crystalline powder, insoluble in water, soluble in alcohol with bluish-violet colour. It is a strong base, taking up carbonic acid from the air, and capable of expelling ammonia from its salts.

It forms three series of salts with acids, and these are exactly analogous to those of the saffranines. The triacid salts are green, and only obtainable with concentrated sulphuric acid. The diacids are blue, and, like the former, are decomposed by water. The monoacid salts are crystalline, have a reddish-violet colour, and are stable.

The mauveine salts do not produce their characteristic reddish-violet colour when dyed on wool, but the shade is the bluer one of the free base.

Hydrochloride, $C_{27}H_{24}N_4,HCl$, forms small lustrous green prisms, sparingly soluble in water, easily in alcohol.

Acetate, $C_{27}H_{24}N_4,C_2H_4O_2$, forms lustrous green prisms.

Carbonate, green prisms with a metallic lustre. Is decomposed on boiling or drying.

Platinum double salt, $(C_{27}H_{24}N_4,HCl)_2PtCl_4$, forms large golden crystals, sparingly soluble in alcohol.

$C_{27}H_{24}N_4(HCl)_2PtCl_4$, dark blue precipitate.

$C_{27}H_{24}N_4,AuCl_3$, crystalline powder.

Ethyl derivative, $C_{27}H_{23}(C_2H_5)N_4$, is formed by action of ethyl-iodide on mauveine in alcoholic solution.

Hydrochloride, $C_{29}H_{28}N_4,HCl$, forms a reddish-brown crystalline powder, sparingly soluble in water, easily in alcohol, forming a purple solution.

$(C_{29}H_{28}N_4,HCl)_2PtCl_4$, golden-green precipitate.

Iodide, $C_{29}H_{28}N_4,HI,I_2$, golden-green crystals.

Pseudomauveine, $C_{24}H_{20}N_4$, is obtained by oxidation of pure aniline, and is very similar to mauveine.

A dyestuff probably identical with pseudomauveine has been obtained synthetically by Fischer and Hepp, by action of paranitrosodiphenylamine on aniline hydrochloride [51].

Hydrochloride, $C_{24}H_{20}N_4,HCl$, green crystals.

Platinum double salt, $(C_{24}H_{20}N_4,HCl)_2PtCl_4$.

The mauveine dyestuffs are formed, although only in small quantities, by oxidation of primary monamines in neutral solution with potassium bichromate, cupric chloride, lead peroxide, and other oxidising agents. It has not been determined with certainty what monamines are capable of yielding dyestuffs of this class; but it is probable that the mauveine $C_{27}H_{24}N_4$ is formed from three molecules of toluidine (ortho and para?) and one molecule of aniline, according to the equation:—

$$3C_7H_9N + C_6H_7N = C_{27}H_{24}N_4 + 10H.$$

It is not certain if the violet coloration obtained with bleaching-powder and aniline solution is due to the formation of mauveine, although this is generally stated.

Mauveine is now of little but historical interest. It was obtained first by Perkin by oxidation of (impure?) allyltoluidine with potassium bichromate. It is still manufactured in small quantities, and used in printing English postage-stamps and for tinting silk for production of white. At present mauveine salts are met with in commerce under the designation Rosolane.

A synthetical process for production of a series of saffranine dyestuffs closely related to mauveine is the subject of a recent patent. It consists in the oxidation of one molecule of paramidodiphenylamine, or one of its homologues, with two molecules of aniline, orthotoluidine, or xylidine [58].

The dyestuffs have a violet colour, and in general closely resemble the mauveines.

Mauveine may be regarded as a phenylated saffranine, $C_{21}H_{19}N_4(C_6H_5)$. Certainly the violet dyestuffs obtained by action of aniline on saffranine are totally different from mauveine, and apparently belong to the Induline series. The fact that mauveine cannot be obtained in this manner is, however, no argument against the assumption that it is a phenylsaffranine, as all these dyestuffs undergo a complete change in constitution on boiling with aniline.

CHAPTER VIII.

ANILINE BLACK.

Most oxidising agents acting in acid solution produce a peculiar dyestuff with aniline salts. This body is characterised by its dark colour, and its sparingly solubility in most solvents. Its formation has been observed by the action of the following agents :—Manganese dioxide [1]; lead peroxide, chromic acid [2]; ferric salts [3]; ferricyanides [3]; permanganates [5]; chloric acid alone [6], or chlorates in presence of certain metallic salts [7], amongst which vanadium, cerium, and copper compounds are the most effective. In all cases these oxidising agents withdraw hydrogen from the aniline molecule.

The formation of aniline black from chlorates and the above-mentioned metallic salts is especially of interest, inasmuch as very small quantities of the latter suffice for the oxidation of relatively large quantities of aniline. Vanadium has the most powerful action in this respect. According to Witz [8], one part of vanadium, aided by the necessary amount of a chlorate, is sufficient to convert 270,000 parts of an aniline salt into aniline black. After vanadium, cerium and copper are the most effective, iron having considerably less action.

It is evident from this that the metallic compounds act only as oxygen-carriers. From the fact that only those metals which form several oxygen or chlorine compounds are capable of producing the desired action, it is probable that the higher metallic oxides effect the oxidation of the aniline, and that these oxides are continuously regenerated by the chlorate present.

If cupric chloride is applied with an insufficient quantity of chlorate, it is possible to detect the formation of cuprous chloride in the mixture. For the production of aniline black from solutions it is necessary that the latter be acid. The formation of black from chlorate and copper salts may, however, take place in presence of excess of aniline, if the mixture be allowed to dry, as is the case in black-printing.

The formation of aniline black from chloric acid and aniline likewise only takes place on drying. Chlorate of aniline is pretty stable in solution, but if the crystallised salt be dried, it is converted into aniline black, which generally retains the crystalline form of the chlorate [33]. Finally, aniline black is formed at the positive pole on the electrolysis of salts of aniline [10, 16].

The substance formed in all these reactions exhibits practically the same properties. It consists principally of a compound of weak but distinctly basic character. The base in the free state has a dark violet, almost black, colour, while its salts are dark green. The latter are unstable and partly decomposed by water. It is, however, difficult to remove the whole of the acid by washing.

The base is almost insoluble in most solvents. It dissolves with difficulty in aniline with a violet colour, which on long standing changes to brown [11].

It dissolves somewhat more easily in phenol, with a bluish-green colour. With concentrated sulphuric acid it forms a violet solution, from which water precipitates the dark green sulphate. With fuming sulphuric acid it yields sulphonic acids differing according to the temperature and duration of the reaction. The sulphonic acids are green in the free state, and form easily soluble salts with the alkalies. These latter have a violet-black colour.

The instability of the salts of aniline black renders it difficult to obtain them with a constant amount of acid. The hydrochloride loses hydrochloric acid on drying, and does not form a definite compound with platinum chloride.

With acetic anhydride, aniline black yields an acetyl derivative, which possesses little colour, and which is insoluble in concentrated sulphuric acid [34].

Methyl and ethyl iodides appear to produce substitution-derivatives, but differ only slightly from the original compound [34]. On treating with potassium bichromate, aniline black gives a violet-black compound, which contains chromic acid and appears to be the chromate of the black base (Chrome-black) [34]. It is not turned green by acids.

Energetic oxidising agents, for example chromic acid in a strongly acid solution, convert aniline black into quinone [34]. Reducing agents form an insoluble leuco-compound, which oxidises slowly in presence of acids, and rapidly in presence of alkalies, aniline black being reproduced.

If the reduction be more energetic,—for example, with tin and hydrochloric acid, or hydriodic acid and phosphorus,—the black is completely split up, paraphenylenediamine, paradiamidodiphenylamine [34], and small quantities of diphenylamine being formed. If the black is submitted to dry distillation, aniline, paraphenylenediamine, diamidodiphenylamine, and diphenylparaphenylenediamine are produced [33].

By continued action of aniline on aniline black, products resembling the indulines are formed. One of these has been isolated, and is a blue dyestuff of the formula, $C_{36}H_{29}N_5$ or $C_{36}H_{31}N_5$ [18].

This substance resembles the indulines, the base having a red colour in alcoholic or ethereal solution, while the salts are blue. It probably bears the same relationship to aniline black as the higher indulines discovered by Witt and Thomas do to the induline $C_{18}H_{15}N_3$. (See page 202.)

The numerous analyses made of aniline black show that it is formed from aniline by simple abstraction of hydrogen. The values obtained approximate nearly to the simple expression, C_6H_5N. Naturally the molecule corresponds to a multiple of this formula, but the instability of the salts has hitherto rendered it impossible to determine the molecular formula accurately.

The following formulæ have been proposed by investigators in this direction :—

1. $C_{12}H_{10}N_2$.
2. $C_{18}H_{15}N_3$.
3. $C_{24}H_{20}N_4$.
4. $C_{30}H_{25}N_5$.

No. 1 was proposed by Kayser [12], No. 3 by Goppelsroeder [15], and Nos. 2 and 4 are due to Nietzki.

Formula No. 4 was based principally on the formation of the above-named blue dyestuff, which was regarded as phenylated aniline black, $C_{30}H_{25}N_5—C_6H_5$. Since then, however, Witt [27] has shown that from the induline $C_{18}H_{15}N_3$ dyestuffs may be produced by the action of aniline, which contain five nitrogen atoms in the molecule, so that this argument for the formula $C_{30}H_{25}N_5$ becomes useless.

Determinations of the amount of hydrogen required to convert aniline black into its leuco-compounds point nearly to two atoms of hydrogen for the formula $C_{18}H_{15}N_3$. This appears to be the correct molecular formula [9]. The fact that the analysis of the black gives throughout slightly lower values for the hydrogen, renders it possible that the formula $C_{18}H_{13}N_3$ may be accurate.

Some conclusions as to the constitution of aniline black are obtained from its decomposition on oxidation and reduction. The production of quinone in the former, and of paraphenylamine, &c., in the latter, render it apparent that the nitrogen atom of one benzene residue enters the chain of another benzene residue in the para position to the nitrogen atom. Goppelsroeder's formula [15], in which the benzene chains are represented as linked in a circle of imido-groups, corresponds to this view to a certain extent. This entirely symmetrical formula, however, does not account for the tinctorial character of the compound in a satisfactory manner; and from the formation of a stable leuco-compound it may be deduced that in all probability at least two nitrogen atoms of the molecule are linked together.

Liechti and Suida [33] regard the black from aniline chlorate as a chlorinated product. This is improbable, as on treating with concentrated sulphuric acid, hydrochloric acid is evolved, and a sulphate almost free from chlorine is produced.

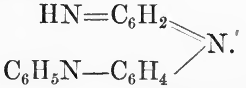
The adoption of similar processes with orthotoluidine results in the formation of a compound probably homologous with aniline black, of the formula C_7H_7N [34].

This compound resembles aniline black in all its properties. The salts are dark green and the free base is bluish black. The latter differs from aniline-black base by the fact that it dissolves in chloroform with a bluish-violet colour [34].

Paratoluidine does not form an analogous compound on oxidation.

Besides the compound described in detail, aniline black generally contains others. One of these is the product of a less energetic oxidation, and is distinguished from the former compound by the brighter green colour of its salts and a brighter violet colour of the free base. It also possesses a considerably higher degree of solubility in alcohol, acetic acid, &c. It dissolves in concentrated sulphuric acid with a red-violet colour. This substance is probably the principal constituent of the dyestuff formerly sold as Emeraldine, and is probably identical with the product formed by oxidation of paraphenylenediamine with diphenylamine [17].

An interesting reaction in which emeraldine is formed was observed by Caro [16]. If aqueous solution of free aniline is oxidised with potassium permanganate, and filtered from the separated manganese dioxide, the filtrate is a yellowish liquid, from which ether takes up a yellow amorphous compound. This latter is converted into a green salt of emeraldine by mere contact with acids. A substance possessing the properties of emeraldine is formed simultaneously with quinone by oxidation of paramidodiphenylamine. A larger yield is obtained if this base is oxidised with an equivalent of aniline, and in this case quinone is not formed [17]. On further oxidation emeraldine yields a darker coloured compound, but it is doubtful if this is aniline black. The formation of emeraldine from paraphenylenediamine and diphenylamine leads to the supposition that it is a phenylated indamine of the formula:



On further oxidation, especially with chlorinating agents, aniline black yields a darker product which is no longer turned green with acids.

On boiling the acetate or the hydrochloride of aniline black with aniline, a mixture of dyestuffs is formed, one of which, a base of the composition $C_{36}H_{29}N_5$, has already been mentioned. The free base dissolves in ether with magenta-red colour; its salts with acids are insoluble in water, soluble in alcohol with a blue colour [18].

$C_{36}H_{29}N_5,HCl$ crystallises from alcohol in small needles which have a coppery lustre.

$(C_{36}H_{29}N_5,HCl)_2PtCl_4$ forms a violet precipitate sparingly soluble in alcohol.

$C_{36}H_{29}N_5,HI$ is similar to the hydrochloride.

$C_{36}H_{29}N_5,C_6H_2(NO_2)_3OH$, sparingly soluble precipitate.

TECHNICAL ANILINE BLACK.

Aniline black in substance is scarcely ever prepared in the colour manufactory, but is always produced directly on the fibre. It has an extended application in calico-printing and cotton-dyeing, but as yet is of little service in wool-dyeing. For aniline-black printing innumerable recipes have been published and patents taken, all depending on one or other of the methods of formation mentioned in the introduction to this chapter.

The oxidising agent most generally employed is potassium (or sodium) chlorate in presence of copper salts [7]. As soluble copper compounds are liable to attack the iron portions of the printing-machine, copper sulphide [19] is used. On printing, this is partly converted into copper sulphate, which then enters into the reaction.

For example, a mixture of aniline hydrochloride, potassium chlorate, and copper sulphide, thickened with starch, is printed. The printed goods are then aged in a moist room, at a temperature of about 30°, and the oxidation of the sulphide to sulphate and of the aniline to black takes place.

Vanadium compounds (vanadic acid and vanadium chloride) have been proposed as substitutes for copper sulphide, but without much practical success. Potassium ferrocyanide and ferricyanide are also used to a certain extent. A mixture of these salts with aniline salt and potassium chlorate is printed, and the goods aged. The probable action is that the ferricyanide oxidises the aniline, and is continually regenerated from the ferrocyanide formed by the chloric acid present. Thus these salts play the part of oxygen carriers in a similar manner to the copper and vanadium compounds. In the opinion of technologists, the black produced by this process differs somewhat in its properties from that obtained with copper, but this may be ascribed to the presence of prussian blue in the former. In place of the aniline hydrochloride and potassium chlorate, a mixture of aniline sulphate and barium chlorate has recently been employed in black-printing.

In printing it is absolutely necessary that the formation of black should not take place in the liquid mixture, as in this case it would soon become useless. Oxidants, like chromic acid, manganese dioxide, &c., which act directly on the aniline, cannot be employed in printing.

In cotton-dyeing, however, the case is just the opposite, as the black formation should be as rapid as possible.

For this purpose the formation of black is often effected by the action between manganese dioxide and aniline salts.

The goods are treated with manganese chloride, and then passed through an alkaline bath whereby manganous oxide is precipitated on the fibre. A subsequent oxidation by air or by a bath of chloride of lime serves to convert this into peroxide, a bottom of the so-called manganese-bronze being obtained. On passing into an acid solution of aniline, aniline black is precipitated on the fibre in a firmly adherent condition.

However, chromic acid is the oxidant generally employed. An aniline solution containing free sulphuric acid is mixed with a soluble bichromate, and the goods entered. On heating, the black is precipitated on the fibre. In all cases the aniline-black salt formed is converted into the free base by a weak alkaline bath (soda, soap, or chalk).

It is merely a matter of conjecture at present if the black produced on the fibre is identical with the products examined in the free state.

The conditions employed in black-printing differ considerably from those when the compound is prepared in substance; for example, the formation of black from aniline salts, chlorates, and metallic salts only takes place in presence of a considerable excess of acid. In printing, on the other hand, an excess is avoided, as it would tend to injure the fibre during the ageing process, and besides would form the black in the liquid printing-mixture.

For this reason an excess of aniline is generally used, and in addition a part of the aniline hydrochloride may be replaced by the tartrate.

Such a mixture does not form black even on long standing; this first takes place when the mass has somewhat dried on the fibre.

In general the oxidation appears to go further than when working in solution.

The black prepared in substance is converted into dark green salts by acids, and this property is often a serious drawback to the black on fibres. This "greening," as it is called, is produced on the goods by acid vapours, for example, by the sulphurous acid produced by the combustion of coal-gas in work-rooms.

This greening may be avoided or, at any rate, reduced to a minimum, by energetic oxidation. The compounds produced in this manner are certainly different from the one described, and are probably its higher oxidation or chlorination products.

Sometimes the goods are submitted to a subsequent treatment to prevent greening. This may consist in passing through a bath of bichromate (formation of aniline-black chromate) or of dilute bleaching-powder.

Aniline black dyed on fibres is one of the fastest colours. It is stable against soap, is only slightly attacked by light and air, and is capable of withstanding a slight treatment with chlorine. More chlorine turns it reddish brown.

CHAPTER IX.

INDULINES AND NIGROSINES.

The dyestuffs included in this classification comprise a series of colouring-matters produced by action of azo-, nitro-, and nitroso-compounds on aromatic amines. They comprise a great variety of shades, from red through blue to almost black.

The indulines are formed in a great number of reactions. Nearly all azo-, azoxy-, and amidoazo-compounds, if heated with salts of aniline or other aromatic amines, produce indulines, and the dyestuffs formed on oxidation of aromatic amines under certain conditions belong in all probability to this class. It is difficult to say with certainty to what extent the products of different reactions are identical with one another.

The nitroso-derivatives of secondary and tertiary aromatic amines also react with aniline and its analogues, producing indulines; and to the study of this reaction and that of the amidoazobenzene process we owe our present knowledge of the composition and structure of the indulines. Researches in this direction have been made by Caro and Dale [21], Martius and Griess [22], Hofmann and Geyger [23], and Fischer and Hepp [35].

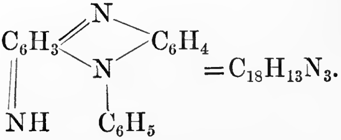
The lower members of the induline series are soluble in water, the higher ones in alcohol.

The nigrosines comprise that section of these dyestuffs produced by action of nitro-compounds on aniline hydrochloride in presence of ferrous chloride. The method employed technically for production of indulines consists in heating aniline hydrochloride with amidoazobenzene. If the reaction be carried out at a low temperature, and especially if the mixture contains an excess of aniline hydrochloride, soluble indulines are produced in larger quantity, while with a protracted reaction insoluble indulines, generally of bluer shade, are formed.

Induline $C_{18}H_{13}N_3$ is formed by heating an amidoazobenzene melt for 10 minutes at 140°. Another induline, $C_{24}H_{18}N_4$, is also formed (see below), and is separated by the less solubility of its acetate in water.

The base, $C_{18}H_{13}N_3$, forms needles with a green metallic lustre, M.P. 135°; the salts are easily soluble in water and dye reddish-violet shades.

The indulines are derivatives of phenazine; the simplest has the constitution:—



From this the higher indulines are formed by introduction of anilido-groups, by phenylation, and by introduction of the rest of paraphenylenediamine. This latter reaction always takes place in a normal induline melt, the paraphenylenediamine being formed from decomposition of amidoazobenzene.

Induline $C_{24}H_{18}N_4$ [36] is produced by operating in a manner similar to above, the temperature of the melt being about 150°. The melt is extracted with a solution of acetate of soda under pressure, whereby the induline, $C_{24}H_{18}N_4$, goes into solution, and the free base precipitated by an alkali. The base forms lustrous leaflets soluble in alcohol with magenta-red colour. The hydrochloride forms bronzy crystals soluble in warm water with a bluish-violet colour. It dyes bluish-violet shades.

Azophenine, $C_{30}H_{24}N_4$, is a constant product of the induline melt and plays an important part, especially in the production of higher indulines. It is formed also by the action of various nitroso-compounds on aniline and aniline hydrochloride, the best result being obtained by paranitrosodiphenylamine. It may be produced synthetically by action of aniline on dianilidoquinone. This synthesis and the production of dianilidoquinone on heating azophenine with sulphuric acid explains its constitution, which is that of a dianilidoquinonedianil:

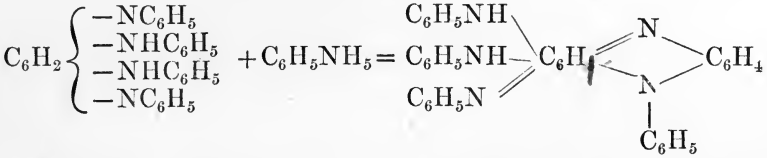
$$C_6H_2\left\{\begin{array}{l} N\,.\,C_6H_5 \\ NH\,.\,C_6H_5 \\ NH\,.\,C_6H_5 \\ N\,.\,C_6H_5 \end{array}\right.$$

Azophenine forms red leaflets, M.P. 240°, which are insoluble in alcohol and ether, but soluble in aniline, benzene, and toluene [27, 28]. On heating the melt containing azophenine, other indulines are formed, amongst which the following, investigated by Witt and Thomas, may be mentioned :—

Induline B, $C_{18}H_{15}N_3$, Azodiphenyl blue.

Induline 3 B, $C_{30}H_{23}N_5$. The hydrochloride is sparingly soluble in alcohol.

Induline 6 B, $C_{36}H_{27}N_5$. This is the best characterised of the induline series. Its hydrochloride forms well-defined crystals which are insoluble in alcohol. Its sulphonic acid dyes wool a pure blue shade. This induline is probably a phenazine produced by action of aniline on azophenine according to the equation [37] :



According to Wichelhaus and v. Dechend induline B is also formed by action of nitrobenzene on aniline hydrochloride, a reaction also observed by Staedeler. An interesting method of obtaining this body is by heating the aniline salt of phenylamidobenzenesulphonic acid (Tropäolin OO). In this case sulphanilic acid splits off. Azodiphenyl blue is also obtained by action of azoxybenzene on aniline hydrochloride [24].

According to Wichelhaus and v. Dechend a new colour-base—Triphenylenediamine, $C_{18}H_{12}N_2$—is formed on heating the hydrochloride of azodiphenyl blue to 230° [24].

On a large scale the indulines are prepared by heating a mixture of amidoazobenzene, aniline hydrochloride, and free aniline to the boiling-point of the latter. Reddish-violet compounds are first formed which gradually change to blue.

The first products of the reaction are simple soluble indulines and azophenine, and from these the higher products are formed by phenylation. In all probability commercial induline contains a mixture of dyestuffs. Paraphenylenediamine and diphenylamine are formed as bye-products in the induline melt.

According to Caro a soluble induline is formed by heating amidoazobenzene hydrochloride with neutral aniline hydrochloride to 100° with a little water [29]. This induline may be fixed on tannined cotton.

An apparently different soluble induline is described by Istel as being formed on heating 2½ parts aniline hydrochloride, 1 part of amidoazobenzene chloride, and 6 parts of water to 70°–80° C. for twenty-four hours. The new dyestuff gives a blue solution with water, and exhibits a reddish-brown fluorescence. It dyes on tannined cotton, and may be also fixed on unmordanted cotton from a bath containing common salt or acetate of soda. The shades on tannined cotton are very fast to light [38].

Indulines have also been prepared technically by heating azobenzene with aniline hydrochloride [25].

Recently a number of patents for the production of soluble indulines have been published. These are based for the greater number on the substitution of a diamine, generally paraphenylenediamine, for the aniline in the usual induline melts. A short summary only of these processes can be given here. The most important of these consists in heating amidoazobenzene hydrochloride with paraphenylenediamine to 180° for three or four hours. A similar product is obtained with amidoazotoluene. The dyestuffs obtained by this process have found technical application, and are known in commerce as Paraphenylene Blues [39, 40].

Metaphenylenediamine may also be used, but the products are not so fast to light. Triamidoazobenzenes (Bismark brown) and Chrysoïdine give soluble indulines on heating with paraphenylenediamine.

Soluble indulines are also obtained:—(1) By heating spirit-soluble indulines, azophenine, quinone, chloranil, azobenzene, azotoluene, or oxyazobenzene with paradiamines (Poirrier). (2) By heating diamidoazoxybenzene with aniline and aniline hydrochloride. (3) By heating nitro-derivatives of the amines with aniline &c. in presence of ferrous chloride. (4) By heating the azo-derivatives of naphthylenediamine [1, 5] with paraphenylenediamine and benzoic acid.

The nigrosines are prepared by heating a mixture of nitrobenzene, aniline, hydrochloric acid, and iron filings to 180°–220°. The colour of the mixture changes through reddish violet to deep blue. They are also prepared by heating a mixture of crude nitrophenol (mixture of ortho and para) with aniline hydrochloride and iron filings. The nigrosines possess a more greyish shade than the indulines, but it is not known with certainty if the colouring-matters are different. A series of similar products to the nigrosines and indulines are formed by oxidation of pure aniline with arsenic acid, but the exact relationship of these dyestuffs one to another is unknown. G. Wolf [31] has published a series of formulæ for these bodies, which cannot, however, be looked upon as trustworthy, as the necessary analytical data are not given.

The violet dyestuffs of magenta residues differ from the indulines in so far that they give a brown solution with sulphuric acid, while all the latter give a blue.

Sulphonic acids of the indulines and nigrosines are also known.

The sodium salts of the sulphonic acids of various indulines come into commerce under the names of Fast Blues, Blackley Blue, Indigo substitute, &c. The difference of the various marks depends on the shade of the induline sulphonated and the number of sulpho-groups introduced.

The indulines are mostly insoluble in water both in form of bases and salts, but are soluble in alcohol. The solutions of the bases are red to reddish violet, the salts are bluish violet, blue, or bluish grey. They are soluble in concentrated sulphuric acid with a pure blue colour, the sulpho-acids have the same colour as the salts of the original induline, and the salts of the sulpho-acids have the same colour as the free bases.

The indulines are destroyed on oxidation, quinone being formed; reducing agents produce easily oxidisable leuco-compounds.

The nigrosines have similar properties.

Spirit-soluble indulines and nigrosines are employed as hydrochlorides, and are principally used for colouring varnishes. Spirit-soluble indulines are applied in printing by a peculiar process. They are printed in combination with tannin and the acetic ethers of glycerine (monoacetine, diacetine); on steaming, these ethers are decomposed, and the liberated glycerine effects the combination of the induline with the tannin and the tannin lake with the fibre (Acetine blue).

Another process for printing consists in the application of a mixture of induline and levulinic acid along with tannic acid, the colour being fixed by steaming [41].

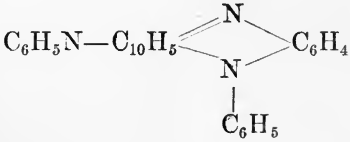
The soluble (sulphonated) indulines are dyed on cotton mordanted with tannin and tartar emetic, a considerable amount of alum being added to the dye-bath. Wool may be dyed directly from an acid bath, the induline generally being used in combination with other acid colours. Silk is dyed in a bath containing boiled-off liquor, the shades being brightened by addition of sulphuric acid.

Soluble indulines of the unsulphonated class are basic dyestuffs, and are principally used in cotton-dyeing on a mordant of tannic acid and tartar emetic.

Rosindulines [42, 43, 44].

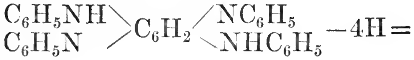
These dyestuffs are indulines of the naphthalene and benzene-naphthalene series.

Nitrosoethyl and nitrosophenylnaphthylamine, if heated with aniline, produce a deep-red dyestuff, and an analogous compound is obtained by heating naphthoquinone and certain of its derivatives with aniline and aniline hydrochloride. The latter dyestuff yields sulphonic acids which dye animal fibres brilliant bluish or brownish-red shades. The sodium salt of one of these acids is known as Azocarmine. The rosinduline from nitrosophenyl and naphthylamine and aniline has the composition $C_{28}H_{19}N_3$. It forms red monoacid and green diacid salts, the latter are decomposed by water. Hydrochloride, $(C_{28}H_{19}N_3HCl)_2 + 1\frac{1}{2}H_2O$, reddish-brown prisms soluble in water and alcohol. Sulphate, $C_{28}H_{19}N_3H_2SO_4 + H_2O$. The constitution of the base may be expressed by the formula :

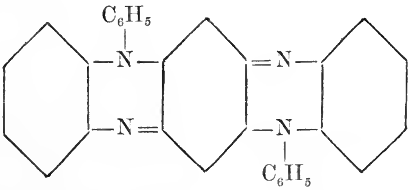


Fluorindines.

These comprise a series of weak dyestuffs discovered by Caro and Witt, the type of which is obtained by heating azophenine with concentrated sulphuric acid or with zinc powder. The formation of this compound, which contains two azine rings, may be represented by the following equation :—



$$\begin{matrix}C_6H_5NH\\ C_6H_5N\end{matrix}>C_6H_2<\begin{matrix}NC_6H_5\\ NHC_6H_5\end{matrix}-4H=$$



Fluorindines are also produced by heating orthodiamines and by heating a mixture of diamidophenazine and orthophenylenediamine [45].

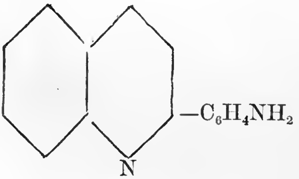
The fluorindines are blue or violet compounds. In sulphuric acid or alcoholic solution they exhibit a magnificent brick-red fluorescence which is very characteristic.

CHAPTER X.

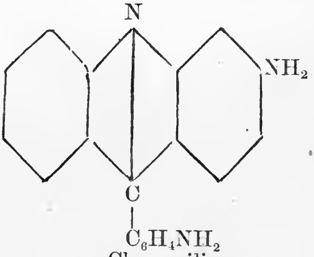
QUINOLINE AND ACRIDINE DYESTUFFS.

Quinoline and Acridine and their homologues belong to the chromogens. The chromogen character is but slight, and is only inconsiderably developed by introduction of amido-groups. The simple amido bases form yellow salts, which are, however, not dyestuffs. These are formed, however, by introduction of an amidated benzene residue.

This is the case with flavaniline and chrysaniline, which are derivatives of phenylquinoline and phenylacridine respectively—



Flavaniline.



Chrysaniline.

Another class of dyestuffs is known in which quinoline does not appear to be the real chromogen. The fact that these bodies cannot be obtained from pure quinoline, but only in presence of its homologues, gives reason for the assumption that they are analogous to the phenylmethane dyestuffs, and that a methane carbon atom links together several quinoline rings.

These dyestuffs include the cyanines, quinoline red, and probably quinoline yellow (?).

Cyanine [2, 3, 4, 5].

On heating a mixture of quinoline and lepidine (methylquinoline) [4] with an alkyl iodide in presence of an alkali, a blue dyestuff is formed, which contains one molecule of each of the bases and the alcohol radical used twice. It is also formed by treating a mixture of the alkyl iodide compounds of quinoline and lepidine with alkali [4]. One molecule of hydriodic acid is split off and the iodide of cyanine formed.

The cyanines are strongly basic compounds; the iodine can only be removed from the iodides by silver oxide.

The monoacid salts are crystalline and of a beautiful blue colour. With weak acids, often even with carbonic acid, they are converted into the colourless di-acid salts [2, 5].

The cyanines dye blue shades, which are, however, too sensitive to light and acids to be of practical value.

Dimethylcyanine [4].—The iodide $C_{21}H_{19}N_2I$ is formed from the methyl iodides of quinoline and lepidine. It forms lustrous green needles, M.P. 291°. Its blue solution is decolorised by carbonic acid. The ethyl iodides of the above bases form the corresponding cyanine iodide $C_{23}H_{23}N_2I$.

An isomeric cyanine is formed if quinaldine is used in place of lepidine [4].

Isoamylcyanine, discovered by Greville Williams [5] and examined later by Hofmann [2], is best known. According to Hofmann it is formed from pure lepidine and possesses the composition $C_{30}H_{39}N_2I$. In all these iodides the iodine may be replaced by other acid radicals.

It is possible that the cyanines are constituted similarly to the phenylmethane dyestuffs, the methyl group of the lepidine furnishing the methane carbon atom. The cyanines belong to the earliest artificial dyestuffs, the first representative having been discovered by Greville Williams in 1856.

Quinoline Red

is obtained by action of benzo-trichloride on coal-tar quinoline in presence of zinc chloride [1, 6]. According to Hofmann's researches there are two different dyestuffs of this class, one of which is derived from quinoline and quinaldine and the other from quinaldine and isoquinoline.

The isoquinoline derivative is easier to prepare and a far better yield is obtained.

The quinoline red from isoquinoline has the composition $C_{26}H_{18}N_2$. It is a base and forms a hydrochloride of the formula $C_{26}H_{18}N_2HCl$. It crystallises in thin quadratic leaflets or in larger prisms. It is sparingly soluble in cold water, easily in hot, and is separated again by an excess of hydrochloric acid.

The platinum double salt has the formula $(C_{26}H_{19}N_2Cl)_2\ PtCl_4$.

On heating quinoline red with ammonium sulphide, benzyl mercaptan is split off, and a compound of the composition $C_{19}H_{14}N_2$ is formed.

On dry distillation it yields a base of the composition $C_{17}H_{15}N$.

Quinoline red may be regarded as analogous in constitution to the triphenylmethane dyestuffs, the methane carbon atom of the benzotrichloride entering into two quinoline residues.

It gives a magnificent eosine-red shade on silk, and exhibits a fluorescence which surpasses that of every other dyestuff. The shades are, however, extremely sensitive to light.

Quinoline Yellow (QUINOPHTHALON) [1, 6].

$C_{18}H_{11}NO_2$.

Is formed by action of phthalic anhydride on quinaldine or on coal-tar quinoline containing quinaldine in presence of zinc chloride. Quinoline yellow crystallises from alcohol in fine yellow needles, M.P. 235°. It is insoluble in water and ether, pretty easily soluble in hot alcohol and glacial acetic acid, and easily in strong sulphuric acid. It has no basic properties and dyes wool and silk yellow. Its sulphonic acid, obtained by treating with fuming sulphuric acid, dyes wool and silk pure yellow like picric acid. Basic dyestuffs may be obtained by heating with ammonia under pressure. Probably these are formed by substitution of oxygen by nitrogenous groups.

The homologues of quinaldine yield similar dyestuffs with phthalic anhydride [7].

A similar dyestuff, pyrophthalon, of the composition $C_{14}H_9NO_2$, is obtained from coal-tar picoline and phthalic anhydride [7].

In all these reactions, phthalic anhydride may be replaced by the anhydrides of the chlorinated phthalic acids.

Owing to its high price quinoline yellow has only found a limited application. It gives very fast shades, and would be valuable in dyeing if the cost of production were less. It is applied solely as sulphonic acid and is dyed like the acid dyestuffs. The shades produced are pure yellow, free from any tinge of red.

Para-amidophenyl-γ-lepidine (*Flavaniline*) [8, 9, 10].

$C_{16}H_{14}N_2$.

This dyestuff is prepared by heating acetanilide with zinc chloride to 250°–270°. The melt is extracted with hydrochloric acid, and the flavaniline precipitated by addition of salt and acetate of soda. The yield is very small.

Flavaniline is a strong base; it forms long colourless needles, sparingly soluble in water, easily in alcohol and benzene, M.P. 97°. It may be distilled without decomposition. The monoacid salts of flavaniline dye wool and silk pretty pure yellow shades.

Hydrochloride, $C_{16}H_{14}N_2,HCl$, forms yellowish-red prisms with a bluish-red reflex. It is easily soluble in water.

Dihydrochloride, $C_{16}H_{14}N_2,(HCl)_2$, is a white salt obtained by adding concentrated hydrochloric acid to the aqueous solution of the former. It is decomposed by water or on heating.

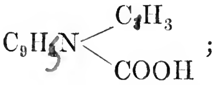
$C_{16}H_{14}N_2 2HCl,PtCl_4$ forms a yellow crystalline precipitate.

Ethyl flavaniline is obtained by action of ethyl iodide on an alcoholic solution of the base.

Iodide, $C_{16}H_{13}N_2(C_2H_5)HI$, forms long ruby-red needles.

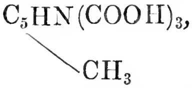
Flavaniline contains an amido-group, and forms a diazo-compound which is converted into flavenol, $C_{16}H_{13}NO$, on boiling with water. This compound exhibits weak basic and acid properties. It forms colourless leaflets, which may be sublimed with partial decomposition, M.P. 128°. It forms colourless salts with acids. On distilling with zinc powder it yields a new base—flavoline, $C_{16}H_{13}N_3$. This latter compound forms colourless lustrous crystals, M.P. 65°. It yields monoacid salts.

The behaviour of flavoline on oxidation shows it to belong to the quinoline series. By oxidation with permanganate it yields first lepidine carbonic acid,



$$C_9H_5N\begin{matrix}CH_3\\COOH\end{matrix};$$

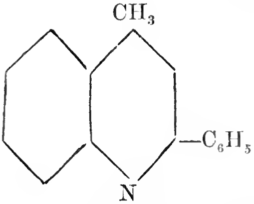
on further oxidation picoline tricarbonic acid,



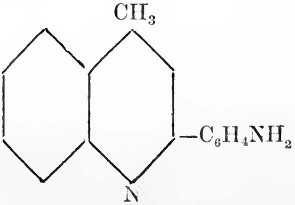
$$C_5HN(COOH)_3, \quad CH_3$$

and finally pyridine tetracarbonic acid, $C_5NH(COOH)_4$.

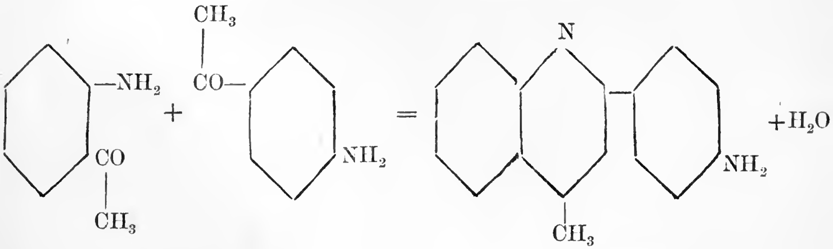
These facts show that flavoline is a methylphenylquinoline:



Flavenol is therefore an hydroxyl- and flavaniline an amido-derivative of this compound. The constitution of flavaniline is expressed by the formula:



An interesting synthesis of flavaniline was effected by O. Fischer. It consists in the condensation of equal molecules of ortho- and para-amidoacetophenone, according to the equation:



Probably the formation of flavaniline from acetanilide and zinc chloride is due to a molecular change of the acetanilide to the isomeric amidoacetophenones, which then form flavaniline.

Berberine.

$C_{20}H_{17}NO_4$.

Berberine is an alkaloid occurring in many plants, and belongs to the quinoline dyestuffs. So far as our present knowledge reaches, it is the only member of this series occurring in nature, and is also the only natural dyestuff with basic properties capable of being fixed on fibres like basic aniline dyes.

Berberine has been found in many plants. The largest quantities are found in Calumba roots (*Cocculus palmatus*) [19], and in the roots of *Berberis vulgaris*, Linn. [20]. The latter is the only one of importance in dyeing.

Pure berberine forms yellow needles, sparingly soluble in alcohol and in water. It loses water of crystallisation at 100° and melts at 120°. It is a monoacid base forming soluble crystalline salts with acids. The nitrate $C_{20}H_{17}NO_4,HNO_3$ is especially noteworthy for the ease with which it forms large crystals; it is insoluble in excess of nitric acid. Berberine is capable of forming lakes with metallic oxides. The dry hydrochloride is turned red by chlorine. On melting with potash it yields quinoline and two acids, one of which, $C_8H_8O_4$, appears to be homologous with proto-catechuic acid [16]. On oxidation with nitric acid, berberine gives pyridine tricarbonic acid [17, 18].

Reducing agents convert berberine to colourless hydro-berberine, $C_{20}H_{21}NO_4$ [16].

In dyeing, berberine is used in form of a decoction of the berberis roots. On animal fibres it is dyed from a neutral bath, and on cotton it is fixed with tannic acid. It is almost exclusively used for dyeing leather.

Chrysanilines.

$C_{19}H_{15}N_3$ and $C_{20}H_{17}N_3$.

The chrysanilines are formed in small quantities as bye-products in the manufacture of magenta, both by the arsenic acid and the nitrobenzene processes. They are separated from the first magenta mother-liquors by partial precipitation with soda, and are finally crystallised from pretty strong nitric acid. The chrysaniline examined by Hofmann [11] has without doubt the formula $C_{20}H_{17}N_3$; but recent researches by Fischer and Koerner [12] render it probable that crude chrysaniline contains two homologous bases, $C_{19}H_{15}N_3$ and $C_{20}H_{17}N_3$. At least the analytical results obtained by Hofmann cannot be brought in unison with the formula $C_{19}H_{15}N_3$ set up by the latter chemists.

The *chrysaniline* $C_{20}H_{17}N_3$ [11], when precipitated from its salts by alkali, forms a light yellow powder similar to precipitated lead chromate. It is almost insoluble in water, dissolves easily in alcohol, benzene, and ether. The two latter solutions exhibit a beautiful yellow-green fluorescence. The base may be distilled with partial decomposition. Chrysaniline forms two series of salts with acids, both of which are yellow to orange in colour. With the exception of the picrate and the hydriodide, the salts are soluble in water, but sparingly soluble in an excess of acid. On dilution, the diacid salts are split up into monoacid salt and water.

Nitrate, $C_{20}H_{17}N_3,HNO_3$, forms orange-yellow needles, sparingly soluble in cold water, easily in hot. From the solution, nitric acid precipitates the *diacid nitrate,* $C_{20}H_{17}N_3,2HNO_3$, in orange-yellow clusters of needles. Chrysaniline is capable of withstanding the action of pretty strong nitric acid.

If impure chrysaniline is dissolved in strong nitric acid, the nitrate crystallises out on standing, and this property is utilised in the purification of the dyestuff.

The *hydrochlorides,* $C_{20}H_{17}N_3,HCl$ and $C_{20}H_{17}N_3,2HCl$, are more easily soluble than the corresponding nitrates.

Picrate, $C_{20}H_{17}N_3 2(C_6H_2(NO_2)_3OH) + H_2O$, forms red needles insoluble in water and sparingly soluble in alcohol.

Trimethylchrysaniline, $C_{20}H_{14}(CH_3)_3N_3$. The dihydriodide, $C_{20}H_{14}(CH_3)_3N_3(HI)_2$, is formed by heating chrysaniline, methyl iodide, and methyl alcohol to 100° for five hours. It forms orange-red needles, soluble in hot water. On adding ammonia to the hot solution, the mono-hydriodide separates in yellow needles. The base may be obtained from these iodides by action of silver oxide. It forms easily soluble salts with most acids.

$C_{20}H_{14}(CH_3)_3N_3(HCl)_2,PtCl_4$ forms yellow felted needles.

The corresponding ethyl derivatives may be obtained in an analogous manner by the action of ethyl iodide. Amyl derivatives have also been prepared [11].

Chrysaniline $C_{19}H_{15}N_3$ [12] was obtained by Fischer and Koerner from commercial chrysaniline. The base crystallises from benzene in clusters of golden-yellow needles, containing one molecule of benzene, which is expelled on drying. It melts at upwards of 200°, and distils with partial decomposition.

Chrysophenol $C_{19}H_{13}N_2O$ [12] is formed by heating the above compound with concentrated hydrochloric acid to 180°.

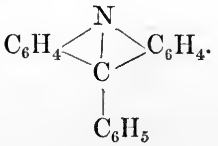
It forms small orange needles, forming salts with acids, and also reacting like a weak acid towards alkalies. It dissolves in soda, forming a light yellow solution from which acids precipitate it as an orange precipitate.

On heating with acetic anhydride, chrysaniline yields a diacetyl compound [13], $C_{19}H_{13}N_3(C_2H_3O)_2$, which still possesses basic properties, forming monoacid salts with acids.

$C_{19}H_{13}N_3(C_2H_3O)_2HCl$ forms long yellow needles, easily soluble in water [13].

The corresponding nitrate is sparingly soluble.

By treating chrysaniline, $C_{19}H_{15}N_3$, with nitrous acid, two nitrogen atoms are converted into diazo-groups. On boiling the resulting diazo-compound with alcohol, phenylacridine is formed:

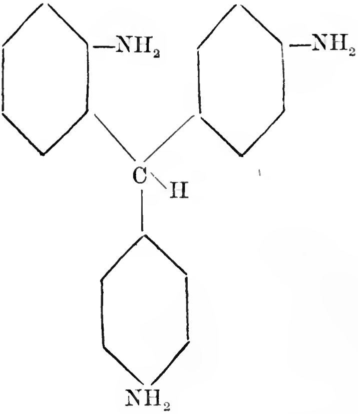


$$\begin{array}{c} N \\ C_6H_4\left\langle\ \Big|\ \right\rangle C_6H_4. \\ C \\ | \\ C_6H_5 \end{array}$$

It follows therefore that chrysaniline is a diamidophenylacridine [12].

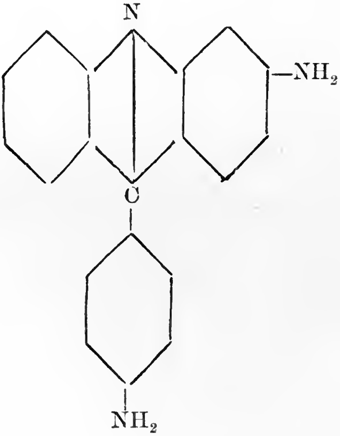
An interesting synthesis of chrysaniline was effected by Fischer and Koerner [12].

Orthonitrobenzaldehyde condenses with aniline to form orthonitroparadiamido-triphenylmethane, which on reduction yields orthodiparatriamido-triphenylmethane:



This compound yields chrysaniline on oxidation.

As in the formation of acridine the nitrogen and carbon atoms take up ortho positions in both benzene-nuclei, chrysaniline has the following constitution :



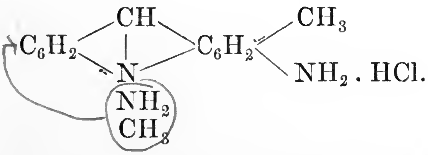
For a considerable period chrysaniline was the only basic yellow dyestuff, and for this reason was largely used in cotton-dying. Wool and silk are dyed directly, cotton requires a tannin mordant. The shade produced is an orange-yellow, noteworthy for its fastness to light.

At present chrysaniline, which is used as nitrate or hydrochloride, under the name of Phosphine, has but a limited application in silk and cotton-dyeing.

The reason for this is that there is no good method for production of phosphine, and as its preparation from magenta-residues is somewhat complicated, its price is relatively high.

Acridine Yellow [22].

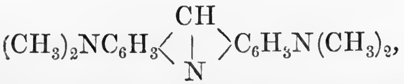
This dyestuff is a hydrochloride of diamidodimethylacridine of the constitution:



For its preparation formaldehyde is condensed with metatoluylenediamine, and the resulting body treated with acid, ammonia splits off, and the resulting leuco-base is oxidised. It dyes silk yellow with green fluorescence.

Acridine Orange.

Acridine orange is according to its formation a tetramethyldiamidoacridine:



$$(CH_3)_2NC_6H_3\left\langle \overset{CH}{\underset{N}{|}} \right\rangle C_6H_3N(CH_3)_2,$$

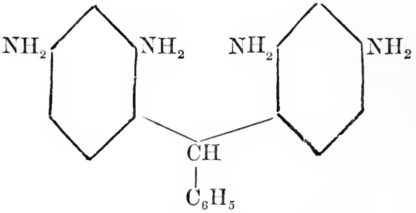
and is obtained by heating of tetramethyltetramidodiphenylmethane with acids and subequent oxidation of the resulting leuco-acridine. Acridine orange is a basic dyestuff producing reddish-orange shades on cotton.

Benzoflavine.

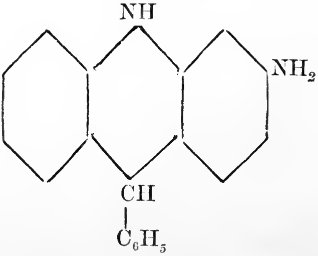
A diamidophenyldimethylacridine isomeric with chrysaniline been brought into commerce under the above name.

According to a patent of C. Oehler, it is obtained in the following manner [21] :—

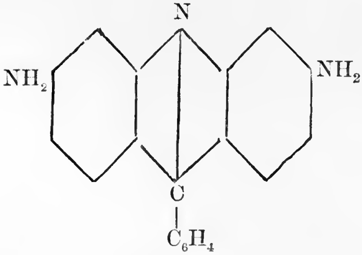
Metaphenylenediamine, or metatoluylenediamine, is condensed with benzaldehyde, forming tetramidotriphenylmethane or its homologues. The latter base on heating with acid loses one molecule of ammonia, yielding diamido-hydrophenylacridine, the leuco-base of benzoflavine, which is formed on oxidation :



Tetramidotriphenylmethane.



Diamidohydrophenylacridine.



Benzoflavine.

Benzoflavine comes into commerce as a yellow powder. It is easily soluble in hot water, and the solution solidifies to a jelly on cooling. From the solution concentrated hydrochloric acid precipitates the sparingly soluble orange hydrochloride. The free base precipitated by an alkali forms a light yellow powder, which dissolves in ether with a beautiful green fluorescence, similar to that of chrysaniline.

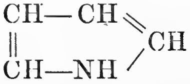
The dyestuff dissolves in concentrated sulphuric acid with a light yellow colour, which becomes orange on dilution.

The shades produced on wool, silk, and on cotton mordanted with tannic acid resemble those with auramine. They may be distinguished by their behaviour towards concentrated hydrochloric acid, benzoflavine becoming orange, while auramine is destroyed. The stability of benzoflavine towards acids is a decided advantage, but it does not appear to be so fast to light as auramine.

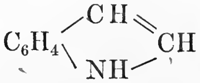
CHAPTER XI.

INDIGO DYESTUFFS.

The colouring-matters of the indigo group, of which the most important is indigo blue, are derivatives of indol. This compound is closely related to pyrrol, both as regards constitution and properties. The relationship existing between indol and pyrrol is analogous to that of benzene to naphthalene, or of pyridine to quinoline, and is best shown by the following formulæ :—



Pyrrol.



Indol.

The nitrogen and carbon atoms of the side ring occupy ortho positions in the benzene ring, and form with the third carbon atom a closed chain containing five members [1, 2].

Indol, like pyrrol, possesses slight basic properties, and also colours a strip of fir, moistened with acid, red. It forms colourless leaflets, M.P. 52°, which have a peculiar, unpleasant smell. It boils at 245° with partial decomposition. With nitrous acid it yields a nitroso-derivative. Of the salts, only the picrate is stable. With acetic anhydride it forms acetylindol.

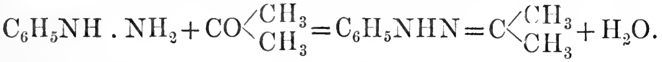
Indol was first obtained by reduction of indigo blue. It is also produced in the pancreatic digestion of albuminoids [2], and by melting the latter with potash.

It may be obtained synthetically by heating orthonitrocinnamic acid with potash and iron filings, and by passing diethylorthotoluidine through a red-hot tube.

Indol is also formed by melting carbostyril with caustic potash [7], by distillation of nitropropenylbenzoic acid with lime [8], by heating orthoamidostyrol with sodium ethylate [9], by passing tetrahydroquinoline through a red-hot tube [10], and by treating orthonitrophenylacetaldehyde with zinc powder and ammonia [11].

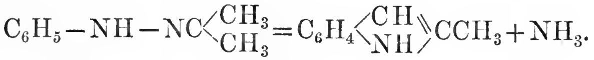
A general synthetic method for production of alkyl-indols is that of Emil Fischer.

Ketones react with phenylhydrazine to produce hydrazones :



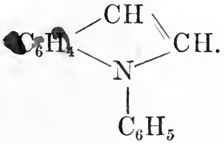
$$C_6H_5NH\ .\ NH_2 + CO\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. = C_6H_5NHN = C\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. + H_2O.$$

The hydrazones, on heating with zinc chloride, split off one molecule of ammonia, with production of a substituted indol:



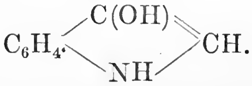
$$C_6H_5 - NH - NC\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle CCH_3 + NH_3.$$

Substituted hydrazines yield the corresponding substituted indols; for example, from diphenylhydrazine and acetone diphenylindol is formed :



DERIVATIVES OF INDOL.

Indoxyl.



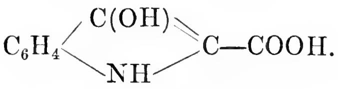
This hydroxy-indol occurs in the urine of herbivorous animals as indoxylsulphuric acid. Indol is converted into indoxylsulphuric acid in the animal organism. From this compound indoxyl is formed by warming with concentrated hydrochloric acid. It may also be obtained by heating indoxylic acid, according to the equation :

$$C_9H_7NO_3 = C_8H_7NO + CO_2\ \ [13].$$

Indoxyl is an oil not volatile in a current of steam. On oxidation it gives indigo blue.

Indoxylsulphuric acid may be obtained by heating indoxyl with potassium pyrosulphate [12]. It exists only in the form of its salts. These are colourless and yield indigo blue on heating or on oxidation.

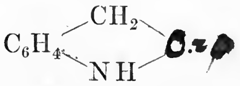
Indoxylic Acid,



The ethyl ether of this acid is formed by reduction of orthonitrophenylpropiolic acid ethyl ether with ammonium sulphide [13].

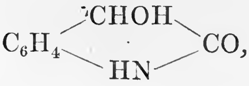
The free acid is obtained by saponification of the ether with an alkali. It forms a crystalline precipitate, sparingly soluble in water. It splits up into indoxyl and carbonic acid on heating. Oxidising agents convert it to indigo blue, while on heating with concentrated sulphuric acid indigo sulphonic acid is formed.

Oxindol [14, 24],



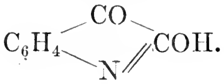
This compound is an inner anhydride of orthoamidophenylacetic acid, and is isomeric with indoxyl. It is formed by reduction of isatin with sodium amalgam [14], and of acetylorthoamidophenylglycollic acid with hydriodic acid [15]. It forms colourless needles, M.P. 120°, and exhibits simultaneously basic and acid properties. It reacts with nitrous acid, producing isatinoxime [24].

Dioxindol,

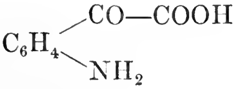


is the inner anhydride of orthoamidophenylglycollic acid. It is the first product of the reduction of isatin with zinc powder [14]. It forms colourless prisms, M.P. 180°. On heating strongly, aniline is formed. It oxidises in aqueous solution, forming first isatyde, and then isatin. Reducing agents convert it to oxindol. Dioxindole is a dibasic acid, but also possesses slight basic properties. Its acetyl derivative is decomposed by baryta water, acetylamidophenylglycollic acid being formed. It yields a nitroso-derivative with nitrous acid.

Isatin.



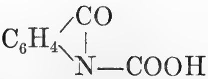
This compound is the inner anhydride of orthoamidophenylglyoxylic acid:



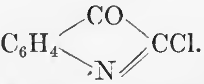
Isatin is formed by oxidation of indigo with nitric acid or chromic acid [16]. It may also be obtained by oxidation of amido-oxindol, and of carbostyril [18], and by boiling orthonitrophenylpropiolic acid with caustic-potash solution. Further methods of formation are given under the synthesis of indigo-blue.

Isatin forms orange prisms, M.P. 200°. It is sparingly soluble in water, easily in alcohol and ether. It possesses the properties of a weak monobasic acid, but also reacts like the aldehydes and ketones; for example, it combines with bisulphites of the alkalies, and with phenylhydrazine and its sulphonic acids [65].

By oxidation with dilute nitric acid it yields nitrosalicylic acid, and on melting with caustic potash, aniline is formed. By oxidation with chromic acid in acetic-acid solution anthranilcarbonic acid (Kolbe's Isatoic Acid) [21] is produced:

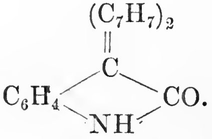


Phosphorus pentachloride converts isatin to isatin chloride:



Isatin forms a blue condensation-product (indophenine) with thiophene. On reduction with ammonium sulphide, isatide $C_{16}H_{12}N_2O_4$ [16] is formed. With zinc powder in acetic-acid solution, isatin yields hydroisatin; by more energetic reducing-agents oxy- and dioxy-indol are formed. Chlorine and bromine react with isatin, forming chlorine and bromine derivatives respectively. Acetic anhydride produces an acetyl isatin [15], probably a derivative of pseudo-isatin. Isatin chloride yields indigo blue on reduction, indigo-purpurin being sometimes formed as a bye-product [22]. Isatin forms ethers with the alcohol radicals. The methyl ether of isatin yields a condensation-product, methyl isatide, $C_{17}H_{12}N_2O_4$. Isatin combines with hydroxylamine, forming an oxime, $C_8H_6N_2O_2$ [25], which is identical with the nitroso-oxindol discovered by Bayer and Knop [14, 24] (pseudo-isatin, see constitution of the Indigo group).

Isatin is capable of yielding condensation-products with hydrocarbons [58]. In the formation of these bodies one oxygen atom of the isatin is replaced by two monovalent hydrocarbon rests. From their behaviour these bodies appear to be derivatives of pseudo-isatin; the toluene derivative has accordingly the formula:



$$\mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{C}{=}(\mathrm{C_7H_7})_2\\ \mathrm{NH}\end{matrix}\right\rangle\mathrm{CO.}$$

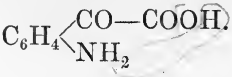
Similar condensation-products may be obtained with tertiary bases and phenols. They yield dyestuffs on oxidation, which probably belong to the triphenylmethane series [58].

The compound formed from isatin and thiophene has the formula:

$$C_{12}H_7NOS \text{ [58].}$$

Indolin, see 62, 63.

Isatic Acid.

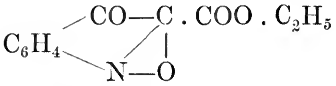


$$\mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{CO{-}COOH}\\ \mathrm{NH_2}\end{matrix}\right.$$

(Orthoamidophenylglyoxylic acid, orthoamidobenzoylformic acid.)

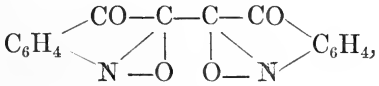
The salts of this acid are formed on heating isatin with a strong solution of caustic alkali. The free acid may be obtained by decomposition of the lead salt with sulphuretted hydrogen [26], or synthetically by reduction of orthonitrophenylglyoxylic acid with ferrous sulphate and caustic soda. The acid is unstable, its aqueous solution decomposes on boiling, isatin and water being formed. Acetylisatic acid is formed by treating acetylisatin with a cold solution of a caustic alkali [15].

Isatogenic Ether [13, 27].



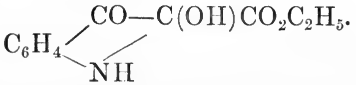
This body is isomeric with the ether of orthonitrophenylpropiolic acid, and is formed on treating the latter with concentrated sulphuric acid. It forms yellow needles, M.P. 115°.

Diisatogen [27],



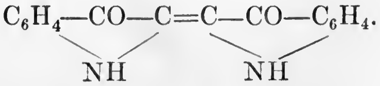
is formed on treating dinitrodiphenyldiacetylene with concentrated sulphuric acid. It forms red needles, soluble only in chloroform, nitrobenzene, and strong sulphuric acid. It is easily converted by reducing agents to indigo blue.

Indoxanthic Ether [28].



This compound is obtained by oxidation of indoxylic ether with ferric chloride. It forms straw-yellow needles, M.P. 107°. Alkalies convert it to anthranilic acid. It forms a nitrosamine with nitrous acid; on reduction indoxylic ether is reproduced.

Indigo-Blue.



Indigo blue is the most important, in fact the only important derivative of indol from a technical point of view.

Indigo occurs as a glucoside, indican, in various plants (*Indigofera tinctoria, Indigofera anil*, *Polygonum tinctorium,* and *Isatis tinctoria*). According to Schunck [29], indican from *Isatis tinctoria* has the composition $C_{26}H_{31}NO_{17}$, and decomposes according to the equation :

$$2C_{26}H_{31}NO_{17}+4H_2O=\underset{\text{Indigo-blue.}}{C_{16}H_{10}N_2O_2}+\underset{\text{Indiglucine.}}{C_6H_{10}O_6}.$$

It is, however, uncertain if the same indican occurs in all plants.

In the industrial preparation of indigo, an aqueous extract of the plants is submitted to fermentation. The indigo blue produced is probably reduced by the sugar, soluble indigo white being formed. On subsequent oxidation in the air, indigo blue separates mixed with various impurities. The crude product obtained in this manner is the valued dyestuff known as indigo. The amount of pure colouring-matter (indigotin) contained in indigo varies, being generally between 20 and 90 per cent. Besides this, it contains various substances : indigo red, indigo brown, indigo yellow, and indiglutin, of most of which but little is known.

Indigotin occurs sometimes in urine.

Indigotin is best obtained from indigo by conversion of the latter into the soluble reduced compound, and subsequent oxidation by air [30] (indigo vat). Another method consists in extracting the indigo with aniline or chloroform and allowing the indigotin to crystallise from the solvent. According to the method of preparation, indigotin forms lustrous coppery needles or a dark blue powder. On heating it does not melt, but sublimes with partial decomposition in form of coppery needles. Indigo vapour has a purple-red colour.

Indigotin is insoluble in most of the usual solvents. It dissolves in aniline, chloroform, nitrobenzene, phenol, paraffin, petroleum, naphthalene, and in certain fatty oils. The solutions have not all the same colour; for example, the aniline and chloroform solutions have a deep indigo-blue colour, while the solution in paraffin has the purple-red colour of indigo vapour, a behaviour somewhat similar to that of iodine.

The composition of indigotin corresponds to the formula C_8H_5NO, but from determination of its vapour-density, the molecule contains twice this and is therefore $C_{16}H_{10}N_2O_2$.

Indigotin dissolves unchanged in concentrated sulphuric acid with a green colour. On heating, sulphonic acids are formed, the colour of the solution changing to blue.

By destructive distillation, indigotin yields aniline; on melting with caustic potash, aniline, anthranilic acid, and salicylic acid are formed [16].

Oxidising agents convert indigotin to isatin [16]. Chlorine produces chlorine derivatives of isatin first, and then chlorinated phenols and chloranil [16]. Bromine acts in a similar manner.

Indigotin dissolves in hot concentrated caustic potash solution with an orange-yellow colour, indigo white and isatic acid being probably formed.

On reduction in alkaline solution indigo blue takes up two atoms of hydrogen, forming indigo white, which possesses phenoloid properties and dissolves in the alkaline liquid.

In the air, indigo white solution oxidises immediately, insoluble indigo blue separating. This property is extensively employed in dyeing with indigo, and also serves for the isolation of pure indigo from the commercial product.

The reducing-agents more commonly employed are ferrous salts, arsenious acid, stannous oxide, hyposulphurous acid, zinc powder, and grape-sugar.

Dibenzoylindigo [32],

$C_{16}H_8N_2O_2(C_7H_5O)_2$,

is formed on heating indigotin with benzoyl chloride.

Halogen derivatives [33] of indigotin have been prepared from the corresponding derivatives of isatin and of orthonitrobenzaldehyde [37].

Dinitro- and diamido-indigotin have been prepared from dinitro-isatin [33]. (Compare the "Synthesis of Indigo Blue," p. 231.)

Indigo White,

$C_{16}H_{12}N_2O_2$,

is formed by reduction of indigotin, and contains two atoms of hydrogen more than the latter. In distinction from indigotin, which possesses neither basic nor acid properties, it exhibits the character of a weak acid like the phenols. It dissolves in alkalies, and may be precipitated from the solutions by an acid. Carbonic acid separates it as a silky greyish-white mass. Indigo white can only be dried and preserved in an atmosphere of carbonic acid or hydrogen. It oxidises rapidly to indigotin on exposure to the air. From the properties of indigo white, it is apparent that the carbonyl oxygen atoms of the indigotin are converted into hydroxyl groups.

From the derivatives of indigo blue (sulphonic acids, &c.), substitution-derivatives of indigo white are obtained on reduction.

Indigo Blue Sulphonic Acids.

Monosulphonic Acid [34],

$C_{16}H_9N_2O_2SO_3H$,

(*Sulphopurpuric Acid.*)

This acid is obtained by heating indigo with concentrated sulphuric acid. It forms purple-red flocks which dissolve in pure water with a blue colour, but are insoluble in dilute sulphuric acid. The salts are sparingly soluble in water, insoluble in saline solutions.

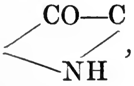
Disulphonic Acid [34],

$C_{16}H_8N_2O_2(SO_3H)_2$,

is formed by further action of sulphuric acid on indigotin. It forms an amorphous powder, soluble in water. The salts are also easily soluble, and may be separated from aqueous solutions by addition of salt. The sodium salt comes into commerce as a paste, and is known as Indigo Extract, Indigo carmine, &c. It is applied like the acid dyestuffs, and has a somewhat extensive application in wool-dyeing. Indigo-disulphonic acid may also be obtained synthetically, the method will be found under Synthesis of Indigotin.

APPLICATION OF INDIGO IN DYEING.

The tinctorial properties of indigo are due to the presence of the chromophorous group:



which forms a closed chain with the benzene ring. As it contains no salt-forming groups it is not a real dyestuff, and owing to its insolubility has no affinity for the fibre. This may be produced by introduction of sulpho-groups, and the indigo then assumes the character of an acid dyestuff. The principal application of indigo depends, however, on its conversion into soluble indigo. The process based on this property is termed vat-dyeing, and has been in use since the earliest periods. Most of the reducing-agents acting in alkaline solution have been applied, but in practice the following are important:—Ferrous sulphate, stannous chloride, grape-sugar, arsenious acid, zinc powder, and sodium hydrosulphite.

The reducing-agent employed is generally added along with lime or soda to a finely divided indigo suspended in water. The ferrous sulphate and stannous chloride are hereby converted to the corresponding hydrates. The indigo blue is slowly converted to indigo white, which dissolves in the alkaline liquid. The indigo-vat is used for dyeing both wool and cotton.

Wool appears to have a certain attraction for indigo white and is capable of withdrawing it from solution, while cotton is only impregnated with the liquid. In all cases the conversion of indigo white to indigo blue on the fibre is effected by atmospheric oxidation. Only in recent years has indigo been applicable for direct printing. Previously calico was dyed in an indigo-vat, and then the necessary effects produced by printing on discharges. Of late years, however, the following methods have been employed on direct printing.

Cotton fabrics impregnated with grape-sugar solutions are printed with a mixture of finely divided indigo and strong caustic soda suitably thickened. On steaming the indigo white produced thoroughly penetrates the fibre, and on oxidation fast indigo effects are obtained.

The difficulties in this direction have also been to a certain extent vanquished by the introduction of artificial indigo. A thickened mixture of orthonitrophenylpropiolic acid and grape-sugar, or better an alkaline xanthate with an alkali is printed, and the indigo blue developed by steaming and drying.

However, orthonitrophenylpropiolic acid does not appear to have made serious competition with natural indigo in this direction, and interesting as the synthesis is from a scientific standpoint, it has not yet been applied practically to any great extent.

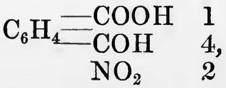
Indigo carmine is almost exclusively used in wool-dyeing, and is applied in an alum bath at the boil.

The shades obtained are finer than those from the vat, but are not so fast. They are principally used in production of mixed shades.

Indigodicarbonic Acid [36],

$C_{16}H_8N_2O_2(COOH)_2$.

This acid is formed by treating nitroterephthalaldehydic acid,



$$C_6H_4\begin{cases} COOH & 1 \\ COH & 4, \\ NO_2 & 2 \end{cases}$$

with acetone and soda solution, and by action of alkali and grape-sugar on the carbonic acid of orthonitrophenylpropiolic acid. It forms a blue precipitate, insoluble in chloroform. The solution with alkalies is green, and is precipitated by acids.

Indoïne [13],

$C_{20}H_{20}N_4O_5$.

Indoïne is formed by reduction of orthonitrophenylpropiolic acid with ferrous sulphate in sulphuric acid solution. It closely resembles indigo, but may be distinguished by the following reactions :—It dissolves in cold concentrated sulphuric acid with a blue colour (indigo gives a green solution), and is only converted into a sulphonic acid with difficulty. It is also easily soluble in aniline and in aqueous sulphurous acid, forming blue solutions.

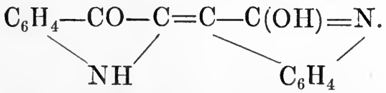
Indigopurpurin.

$C_{16}H_{10}N_2O_2$.

This compound is isomeric with indigotin, and is formed as a bye-product in the preparation of the latter from isatin chloride [22, 38].

It is similar to indigotin, but is more readily sublimed, forming fine red needles. It dissolves in alcohol with a red colour. On dissolving in concentrated sulphuric acid and diluting with water, it gives a red solution.

Indirubin [13, 60].



$$\underset{\diagdown\quad NH \quad\diagup}{C_6H_4-CO-C}=\underset{\diagdown\quad C_6H_4 \quad\diagup}{C-C(OH)=N.}$$

Indirubin is the indogenide of isatin, and is isomeric with indigotin. It may be obtained by mixing aqueous solutions of indoxyl and isatin in presence of a little caustic soda.

Indirubin forms a reddish-brown powder. It dissolves in alcohol with a violet colour, and in concentrated sulphuric acid with a greyish-black colour. The latter solution becomes violet on heating, a sulphonic acid being formed. With reducing-agents gives a vat, and on further reduction indileucin, $C_{16}H_{12}N_2O$, is produced.

From the present state of our knowledge, it is not certain if indigopurpurin and indirubin are identical or different.

Indigo Red [61].

This compound, which occurs in crude indigo, is also an isomer of indigotin. The exact relationship existing between this body and the two previous ones is not certain. According to Baeyer, it differs from indigopurpurin.

Schunck obtained a compound from indican which he named Indirubin, and which he regards as identical with indigo-purpurin [61].

Indigo red forms a vat and a sulphonic acid, both capable of dyeing. The shades produced in the vat are noteworthy for their extreme fastness to light.

SYNTHESIS OF INDIGO BLUE.

In the years 1865 and 1866 Baeyer and Knop [14] converted indigotin through dioxindol and oxindol into indol; and three years later Baeyer and Emmerling [5] prepared indol synthetically by melting a mixture of nitrocinnamic acid, caustic potash, and iron filings. The nitrocinnamic acid employed was a mixture of the ortho and para compounds, and only later was it discovered that the ortho acid is alone capable of yielding indol. In 1870 the same chemists observed the formation of indigo blue by treating isatin with a mixture of phosphorus trichloride and acetyl chloride.

In the same year Emmerling and Engler [39] obtained small quantities of indigo by heating nitroacetophenone with zinc powder and soda-lime, but subsequently were unsuccessful in producing the necessary conditions for the formation of the dyestuffs.

The first certain method for producing artificial indigo is due to Nencki, who obtained it by oxidation of indol with ozone [40]. The same chemist had already obtained indol by the pancreatic fermentation of albumen [2, 40]. In 1877 Baeyer and Caro obtained indol by passing the vapour of certain aromatic amines, especially of diethylorthotoluidine, through a red-hot tube.

In 1878 the constitution of oxindol was discovered by Baeyer [17] and by Suida [15]. It was found to be the inner anhydride of orthoamidophenylacetic acid, and was obtained synthetically from the latter.

In the same year [17] Baeyer prepared isatin from oxindol. The nitroso-compound of oxindol yields the amido-compound on reduction, and this is converted into isatin by oxidation or by nitrous acid.

As isatin had already been converted into indigo, the formation of the former from orthoamidophenylacetic acid effects a complete synthesis of indigo. At the same time Baeyer [17] improved the process whereby isatin was converted into indigo.

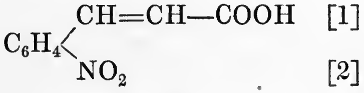
Isatin is first submitted to the action of phosphorus tri- or pentachloride, and the resulting isatin chloride yields indigotin on reduction. In this case indigopurpurin is formed as a bye-product.

Claisen and Shadwell discovered a new synthetical method for production of isatin in 1879. By action of silver cyanide on orthonitrobenzoyl chloride, orthonitrobenzoyl cyanide is produced, and this is converted into orthonitrophenylglyoxylic acid by saponification and subsequent treatment with an alkali. On reduction of this acid in alkaline solution, a salt of isatic acid (orthoamidophenylglyoxylic acid) is produced, from which isatin may be separated by an acid.

These researches effect another complete synthesis of indigotin.

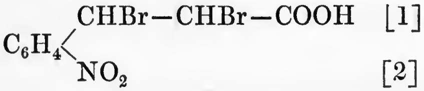
In 1880 Baeyer prepared indigo synthetically from cinnamic acid by various processes [19, 41] :—

I. Orthonitrocinnamic acid,



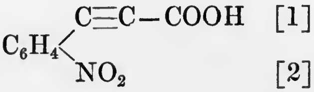
$$C_6H_4\Big\langle\begin{matrix} CH{=}CH{-}COOH & [1] \\ NO_2 & [2] \end{matrix},$$

unites with bromine to form orthonitrodibromhydrocinnamic acid,



$$C_6H_4\Big\langle\begin{matrix} CHBr{-}CHBr{-}COOH & [1] \\ NO_2 & [2] \end{matrix}.$$

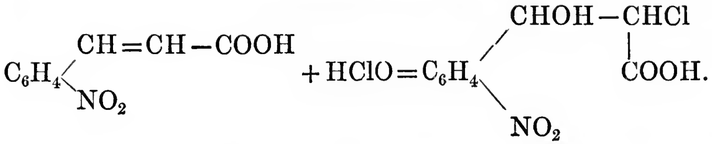
On treating this compound with alkalies, two molecules of HBr split off and an unsaturated acid—orthonitrophenylpropiolic acid,



$$C_6H_4\Big\langle\begin{matrix} C{\equiv}C{-}COOH & [1] \\ NO_2 & [2] \end{matrix},$$

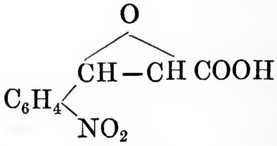
is formed. This acid yields isatin on boiling with an alkali, and indigo on reduction in an alkaline solution (alkaline grape-sugar solution, or an alkaline xanthate).

II. By treating orthonitrocinnamic acid with chlorine in alkaline solution, orthonitrophenylchlorlactic acid is formed according to the equation :—



$$C_6H_4\left\langle\begin{array}{l}CH=CH-COOH\\NO_2\end{array}\right. + HClO = C_6H_4\left\langle\begin{array}{l}CHOH-CHCl-COOH\\NO_2\end{array}\right.$$

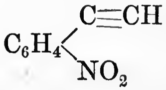
This acid gives orthonitrophenyloxyacrylic acid on treating with an alkali,



$$C_6H_4\left\langle\begin{array}{l}\overbrace{CH-CH}^{O}\,COOH\\NO_2\end{array}\right.$$

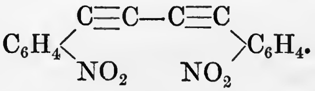
On heating in phenol, or glacial acetic-acid solution, this compound yields indigo.

III. Orthonitrophenylpropiolic acid yields orthonitrophenylacetylene on boiling with water [42]:



$$C_6H_4\left\langle\begin{array}{l}C\equiv CH\\NO_2\end{array}\right.$$

On oxidation of the copper compound of the latter with potassium ferricyanide, dinitrodiphenyldiacetylene is produced:



$$C_6H_4\left\langle\begin{array}{ll}C\equiv C- & C\equiv C\\NO_2 & NO_2\end{array}\right\rangle C_6H_4.$$

On treatment with fuming sulphuric acid this body undergoes a molecular change, an isomer, diisatogen, being formed. The latter gives indigo on reduction [42].

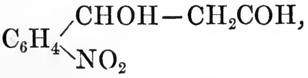
IV. In 1882 orthonitrobenzaldehyde was used as a starting-point for the artificial production of indigotin [2].

On dissolving orthonitrobenzaldehyde in acetone and adding an excess of dilute caustic-soda solution, indigo blue separates on standing. The acetone may be replaced by acetaldehyde or pyruvic acid. This reaction was studied in detail by Baeyer [44]. The interaction of acetone and orthonitrobenzaldehyde results in the formation of an intermediate product of the composition $C_{10}H_{11}NO_4$ (probably the methyl ketone of orthonitrophenyl-lactic acid). This compound decomposes under the influence of alkalies according to the equation:

$$2C_{10}H_{11}NO_4+2H_2O=C_{16}H_{10}N_2O_2+2C_2H_4O_2+4H_2O,$$

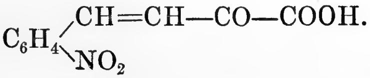
indigotin and acetic acid being formed.

With acetaldehyde, orthonitrobenzaldehyde forms the aldehyde of orthonitrophenyl-lactic acid :



$$C_6H_4\begin{array}{l}\diagup CHOH-CH_2COH, \\ \diagdown NO_2\end{array}$$

which splits up with alkalies, forming indigotin and formic acid [45]. The intermediate product in the case of pyruvic acid is orthonitrocinnamyl-formic acid [44] :



$$C_6H_4\begin{array}{l}\diagup CH{=}CH-CO-COOH. \\ \diagdown NO_2\end{array}$$

This body is best obtained by action of gaseous hydrochloric acid on a mixture of the reacting compounds. Orthonitrocinnamylformic acid is split up by alkalies into indigotin and oxalic acid.

A patent of Meister, Lucius, & Brüning [46] depends on a similar reaction. Claisen's benzylidene-acetone (cinnamylmethylketone $C_6H_5-CH=CHCO-CH_3$) [47], obtained by condensation of benzaldehyde and acetone, is nitrated. A mixture of ortho and paranitro derivatives is formed, and the former yields indigotin by action of alkalies.

Ortho-nitrometa-tolualdehyde [48] gives a homologue of indigo-blue, and chlorine derivatives may be obtained from chlor-ortho-nitroaldehydes [37]. Another method has its starting-point in ortho-amidoacetophenone. This compound is converted into its acetyl derivative and treated with bromine in the cold. The resulting bromine derivative, when dissolved in concentrated sulphuric acid, loses hydrobromic acid, a crystalline compound being formed, which, under the influence of air in presence of alkalies, yields indigotin.

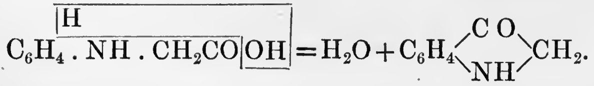
Indigotin may also be obtained from ortho-amidophenylacetylene by an analogous process.

Gevekoht [50] obtained indigotin by action of ammonium sulphide on ortho-nitroacetophenone, in which the methyl group is brominated.

From the researches of Baeyer [51] and Bloem it is shown that on brominating acetylortho-amidoacetophenone, the bromine atom enters in the methyl group. If the benzene chain is substituted brominated indigos are formed; but if only the benzene chain contains bromine, indigo cannot be produced. In these reactions indoxyl appears to be formed as an intermediate product in the reaction.

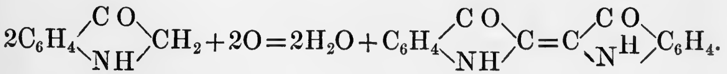
P. Meyer [52] prepared substituted indigo blues from the corresponding substituted isatins. This process depends on the fact that the final products of the action of dichloracetic acid on amines in which the para position is occupied are substituted isatins. The first product of the action of dichloracetic acid on paratoluidine is a paratolylimide derivative of paramethylisatin, $C_{16}H_{16}N_2O$, which decomposes on boiling with acids into paratoluidine and methylisatin, $C_9H_7NO_2$.

Perhaps the simplest methods for the synthetic production of indigo are those which have their starting-point in certain aniline derivatives of acetic acid. Flimm discovered that bromacetanilide, $C_6H_5NH—CO—CH_2Br$, gives a trace of indigo on heating with caustic potash (B. B. 1890, p. 57). Heumann's process gives a somewhat better result, but still the yield (about 15 per cent.) is not sufficiently great for technical application. In this method phenylglycocine, formed by action of monochloracetic acid on aniline, is heated with caustic potash with exclusion of air to about 260°. The orange-yellow melt obtained is dissolved in water, and on exposure to air indigo separates. The course of the reaction is not exactly understood, but in all probability the first stage consists in the formation of pseudoindoxyl:



$$C_6\overset{|H}{H_4} . NH . CH_2CO\boxed{OH} = H_2O + C_6H_4{<}\begin{matrix}CO\\NH\end{matrix}{>}CH_2.$$

In alkaline solution pseudoindoxyl oxidises immediately, producing indigo:



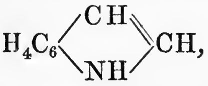
$$2C_6H_4{<}\begin{matrix}CO\\NH\end{matrix}{>}CH_2 + 2O = 2H_2O + C_6H_4{<}\begin{matrix}CO\\NH\end{matrix}{>}C=C{<}\begin{matrix}CO\\NH\end{matrix}{>}C_6H_4.$$

A somewhat better result is obtained by using phenylglycocine-orthocarbonic acid, which is prepared by action of monochloracetic acid on anthranilic acid. This compound is fused with caustic potash, the reaction taking place at a considerably lower temperature than when phenylglycocine is employed.

If phenylglycocine is mixed with sand and introduced into a large quantity of sulphuric acid containing a considerable amount of sulphuric anhydride, taking care to avoid an increase in temperature, a reaction immediately takes place, sulphurous acid being evolved, while the solution takes a blue colour. This is due to the formation of indigo-disulphonic acid, which may easily be isolated by dilution and addition of salt. The yield by this process is satisfactory, amounting to about 60 per cent. of the phenylglycocine used.

CONSTITUTION OF THE INDIGO GROUP.

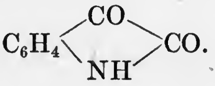
From his synthesis of indol from orthonitrocinnamic acid Baeyer ascribed to it the constitutional formula:



$$H_4C_6 < \begin{matrix} CH \\ NH \end{matrix} > CH,$$

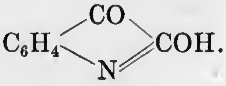
which is now generally accepted.

Kekulé had already (1869) [53] published an opinion that isatin is an inner anhydride of orthoamidophenylglyoxylic acid, and accordingly suggested the structural formula:



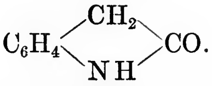
$$C_6H_4 < \begin{matrix} CO \\ NH \end{matrix} > CO.$$

Claisen and Shadwell proved that isatic acid is orthoamidophenylglyoxylic acid, and that isatin is its inner anhydride by a direct synthesis [26]. However, various properties of isatin noted by Baeyer speak for the presence of an hydroxyl group according to the formula:

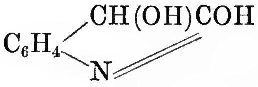


$$C_6H_4 < \begin{matrix} CO \\ N \end{matrix} \gg COH.$$

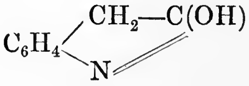
Oxindol is, from its synthetic production, an inner anhydride of orthoamidophenylacetic acid, and has the formula :



The formation of oxindol and dioxindol by reduction of isatin is, however, more in favour of the following constitution for these compounds :—

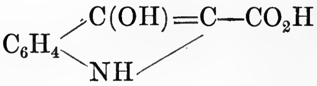


Dioxindol.

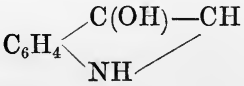


Oxindol.

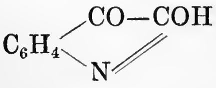
The constitution of indoxyl may be deduced by its formation from indoxylic acid :



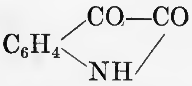
The hydroxyl group must be in combination with the carbon atom in the adjacent position to the benzene ring. The constitution of indoxyl is accordingly represented by the formula



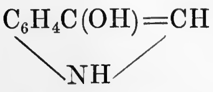
From certain reactions it appears probable that isatin, indoxylic acid, and indoxyl are capable of existing in two isomeric forms. One of these exists only in the form of derivatives (for example, ethers). Baeyer terms these " labile or pseudo forms," and gives the following formulæ to them :—



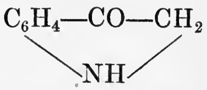
Isatin.



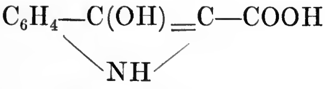
Pseudoisatin.

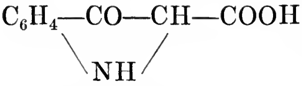


Indoxyl.

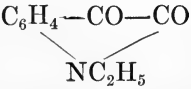


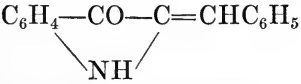
Pseudoindoxyl.


Indoxylic acid.

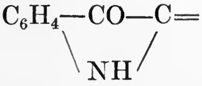

Pseudoindoxylic acid.

These pseudo-modifications are stable when certain of their hydrogen atoms are replaced. In the case of pseudoisatin a monovalent group suffices; while in pseudoindoxyl both hydrogen atoms of the carbon atom in the side-ring must be replaced. In this manner the following compounds may be obtained:—


Ethylpseudoisatin.

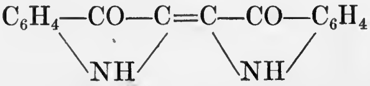

Benzylidenepseudoindoxyl.

The divalent rest of pseudoindoxyl,

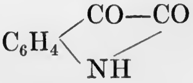


is especially interesting, as researches on this subject show that it must be contained in indigotin. Baeyer designates this rest as the indogene group, and those derivatives in which the indogene group replaces an atom of oxygen are termed indogenides. The above benzylidenepseudoindoxyl must therefore be regarded as the indogenide of benzaldehyde, as it is formed by heating indoxylic acid with benzaldehyde, carbonic acid and water splitting off.

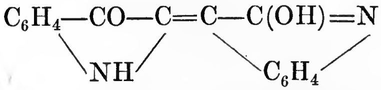
Indigotin may be regarded as a combination of two indogene groups, as expressed by the constitutional formula:


Indigotin.

This constitution is also that of an indogenide of pseudoisatin:


;

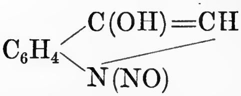
and indigotin is therefore formed by replacement of an oxygen atom of pseudoisatin by the indogene group. Similarly, indirubin is the indogenide of isatin:



Indirubin is formed by action of isatin on indoxyl, in which reaction it must be accepted that the latter undergoes a molecular change into pseudoindoxyl.

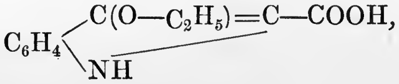
Baeyer arrives at these conclusions from the following facts:—

By the action of nitrous acid on indoxyl a nitrosamine of the latter is formed:



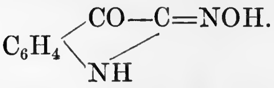
On reduction it is converted through indoxyl to indigotin. By action of nitrous acid on ethylindoxylic acid [56] an isomeric compound, possessing the properties of an isonitroso compound, is formed. It yields isatin on reduction and subsequent oxidation.

It is probable that in the formation of this body from ethylindoxylic acid:



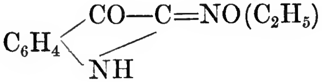
a molecular change takes place, as two monovalent groups are split off from two different carbon atoms, and the isonitroso group is always divalent and connected with one carbon atom.

The formation of isatin from this body shows it to be pseudisatoxime or isonitrosopseudoindoxyl:

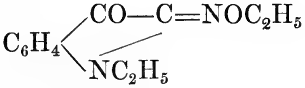


This constitution receives further support from the behaviour on ethylation, whereby a mono-ethyl ether is produced. This ether also yields isatin, and therefore cannot contain the ethyl group in direct combination with a carbon atom, nor yet in the imide group. It is stable to hydrochloric acid, which would not be the case were the ethyl group connected with hydroxyl.

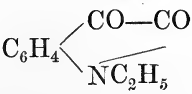
The constitution of the compound is therefore expressed by the formula :



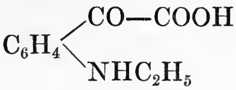
It is pseudoisatinethyl-*a*-oxime. On further ethylation the diethyl ether is formed :



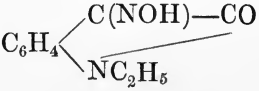
On reduction and subsequent oxidation, ethylpseudoisatin is formed :



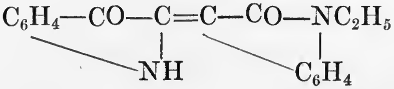
It differs from the isomeric ethylisatin by being difficult to saponify. Alkalies convert it to ethylisatic acid :



With hydroxylamine ethylpseudoisatin gives the *β*-oxime

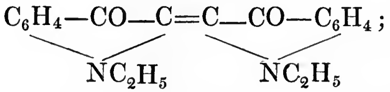


It combines with indoxyl to form the indogenide



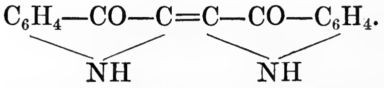
The diethyl ether of pseudoisatin-*a*-oxime yields diethyl indigo blue if treated with mild reducing-agents, precisely in the same manner that pseudoisatoxime gives indigo blue under similar conditions.

As in this reaction the ethylated isonitroso group is split off, while the ethyl group attached to the imide-nitrogen atom remains intact, it follows that if the above constitution of ethyl pseudoisatin ethyl *α*-oxime is correct, diethyl-indigotin must possess the constitution expressed by the formula:



$$\begin{array}{c}C_6H_4\text{—}CO\text{—}C{=}C\text{—}CO\text{—}C_6H_4\,;\\ NC_2H_5 \qquad\qquad NC_2H_5\end{array}$$

and consequently indigotin the analogous one:



$$\begin{array}{c}C_6H_4\text{—}CO\text{—}C{=}C\text{—}CO\text{—}C_6H_4.\\ NH \qquad\qquad NH\end{array}$$

Baeyer summarises the conclusions leading to this formula as follows:—

1. Indigotin contains an imido-group.

2. Its formation from diphenyl-diacetylene shows that the carbon atoms are placed in the following manner:—

$$C_6H_5\text{—}C\text{—}C\text{—}C\text{—}C\text{—}C_6H_5.$$

3. Indigotin is formed only from those compounds in which the carbon atom adjacent to the benzene ring is connected with an atom of oxygen.

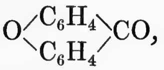
4. The formation and properties of indigotin show a close relationship to indirubin and to the indogenide of ethylpseudoisatin. The latter is formed by the coupling of the *α*-carbon atom of pseudoindoxyl with the *β*-carbon atom of pseudoisatin.

CHAPTER XII.

EUXANTHIC ACID AND GALLOFLAVINE.

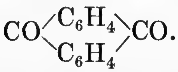
THESE yellow dyestuffs, though of totally different origin, show some relationship in chemical properties, and possibly owe their tinctorial value to the same chromophor. In euxanthic acid this is a carbonyl group, which forms a ring with one oxygen atom and two benzene nuclei.

Euxanthic acid contains as chromogen the rest of diphenylene-ketone-oxide:



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

somewhat similar in constitution to anthraquinone,



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

It has not been determined with certainty that galloflavine contains the same group.

Euxanthic Acid.

$C_{19}H_{18}O_{11}$.

The magnesium salt is the essential constituent of the dyestuff known in commerce as Purrée or Indian Yellow. This product is obtained from the urine of cows, fed on mango-leaves. The gold-yellow urine is heated, and the yellow deposit formed into a ball. This is purified by removing the outer portions and thoroughly washing the remainder.

The recent researches of v. Kostanecki [8] demonstrate that the origin is from urine, as they proved that the urine of animals whose food contained euxanthone separated euxanthic acid. It is probable that the euxanthone contained in certain plants combines with glucuronic acid in the animal organism, euxanthic acid thus being formed. To prepare euxanthic acid, purrée is exhausted with water, treated with dilute hydrochloric acid, and the residue extracted with ammonium carbonate. The resulting ammonium salt is decomposed with hydrochloric acid, and the euxanthic acid crystallised from alcohol (2).

It forms lustrous straw-yellow needles, sparingly soluble in cold water, more easily in hot water, and readily in alcohol, but insoluble in ether.

On heating to 130° one molecule of water splits off, an anhydride, $C_{19}H_{16}O_{10}$ [6], being formed. This was formerly regarded as anhydrous euxanthic acid, the crystallised acid having the formula $C_{19}H_{16}O_{10} + H_2O$. Euxanthic acid is monobasic; its salts with the alkalies are easily soluble, those with magnesium and lead sparingly soluble. The alkali salts are precipitated by an excess of alkali. On heating with water or dilute sulphuric acid to 140°, euxanthic acid splits up into euxanthone [1], $C_{13}H_8O_4$, and glucuronic acid, $C_6H_{10}O_7$ [6].

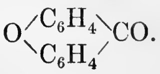
Euxanthone is also formed by heating euxanthic acid to 160–180°, or by warming with concentrated sulphuric acid [38].

Chlorine and bromine act on euxanthic acid, producing di-substitution products [2]. Nitric acid produces nitro-euxanthic acid in the cold; on warming, trinitro-euxanthone, and finally styphnic acid is formed [1].

Euxanthone.

$C_{13}H_8O_4$.

This compound forms pale yellow needles which sublime without decomposition. It is insoluble in water, sparingly soluble in ether, easily in boiling alcohol. It is formed as described above from euxanthic acid, and is also a constituent of purrée, the lower qualities containing most. It is soluble in aqueous solutions of the alkalies, but possesses no further acid properties. Its alcoholic solution is precipitated by lead acetate. On heating with zinc powder, benzene, phenol, and methylenediphenylene-oxide, $CH_2-(C_6H_4)_2O$ [9], are formed. The last-named compound yields diphenyleneketone-oxide on oxidation,

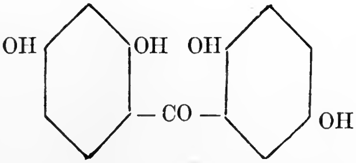


$$O\begin{matrix}\diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup\end{matrix}CO.$$

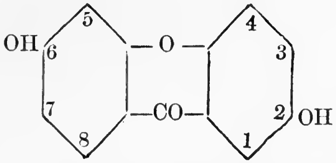
Diacetyleuxanthone is formed on boiling euxanthone with acetic anhydride, M.P. 185°. Dichloreuxanthone and dibromeuxanthone may be produced by decomposition of the corresponding derivatives of euxanthic acid [2].

Trinitroeuxanthone forms yellow needles, and is a monobasic acid [2].

The constitution of euxanthone is explained by the following researches of Baeyer and Graebe [21]. On melting with potash it yields euxanthonic acid (tetraoxybenzophenone),



which on further heating splits up into resorcin and hydroquinone. Euxanthone is the inner anhydride of euxanthonic acid,



and is therefore 2.6 dioxydiphenyleneketone-oxide. This is confirmed by its synthesis, on heating hydroquinone carbonic acid with β-resorcylic acid in presence of acetic anhydride.

Euxanthic acid is apparently an ether of euxanthone (or euxanthonic acid) with glucuronic acid.

$$C_{13}H_8O_4 + C_6H_{10}O_7 = C_{19}H_{18}O_{11}.$$

Euxanthone. Glucuronic acid. Euxanthic acid.

Euxanthone, although yellow, is not a dyestuff, while euxanthic acid is capable of dyeing on metallic mordants.

Its principal application is as an artists' pigment under the name of Indian Yellow.

SYNTHETICAL OXYKETONE DYESTUFFS [22].

A method for the production of hydroxyl derivatives of benzophenone and its homologues has been patented by the Badische Anilin- und Sodafabrik.

The process consists in heating fatty or aromatic acids with a phenol or oxycarbonic acid containing at least two hydroxyl groups in the ortho position to each other with a dehydrating agent. The reaction may be best explained by the following example.

Trioxybenzophenone.

One part of pyrogallol and one part of benzoic acid are heated to 145°, and three parts of zinc chloride gradually stirred into the mixture, and the above temperature maintained for three hours. The melt is extracted with boiling water, and on cooling the dyestuff is deposited in yellow needles, M.P. 137–138°. It dyes golden-yellow shades on cotton mordanted with alumina; the presence of lime-salts renders the tone more orange. Another process for production of trioxybenzophenone, due to the same firm, consists in heating pyrogallol with benzotrichloride in aqueous, alcoholic, or acetic acid solution. It is known in commerce as Alizarin Yellow A.

Gallacetophenone.

This compound is a trioxyacetophenone $\{(OH)_3C_6H_2COCH_3\}$, obtained by heating pyrogallol with acetic acid and zinc chloride to 150°. It may be used for printing with chromium acetate, and gives brown shades [23]. It is named Alizarin Yellow G.

Ellagic Acid.

$C_{14}H_8O_9$.

This compound is related to the above dyestuffs and to galloflavine, although its constitution has not been determined with certainty. Ellagic acid may be obtained by action of various oxidising agents on gallic and tannic acids, and by heating gallic ether with soda solution. It also occurs naturally in bezoar stones. Ellagic acid gives greenish-yellow shades when printing with chromium acetate.

Galloflavine.

This dyestuff is formed by oxidation of a gallic acid solution, containing about two molecules of an alkali, by atmospheric oxygen [12]. It is best prepared by dissolving gallic acid in alcoholic potash solution, and passing a current of air through the solution. A potassium salt of the dyestuff, which is sparingly soluble in alcohol, separates [11].

Galloflavine forms greenish-yellow leaflets, sparingly soluble in ether and alcohol, more easily in acetic acid, and best in aniline. It is soluble in alkalies, and is reprecipitated on the addition of acids.

The composition of galloflavine is probably represented by the formula $C_{13}H_6O_9$.

It forms dibasic salts; those with the alkalies are easily soluble in water.

If heated with acetic anhydride, it yields a colourless acetyl compound, $C_{13}H_2O_9(C_2H_3O)_4$, M.P. 230° [11].

Galloflavine is used along with metallic mordants. On alumina it produces a greenish-yellow shade, on tin oxide a pure yellow, and on chromium oxide an olive-green. It has been used to a slight extent in wool-dyeing; on chromed wool it gives results similar to fustic.

CHAPTER XIII.

CANARINE. [13, 14, 15.]

On treating potassium sulphocyanide with potassium chlorate, in presence of hydrochloric acid, canarine is formed (Prokoroff and Miller) [13].

This compound is probably identical with that discovered by Liebig [16], and named pseudo- or persulpho-cyanogen, $C_3N_3HS_3$, although the identity of the two is denied by Miller.

Canarine forms a yellow powder, insoluble in neutral solvents, soluble in alkalies and in borax solution.

The application of canarine depends on its property of dyeing cotton yellow from an alkaline solution. The shades vary from light yellow to orange-yellow, according to the concentration of the solution. They are very fast both to soap and light. In comparison with other artificial dyestuffs, canarine only possesses weak tinctorial properties.

Canarine dyed on cotton is capable of acting as a mordant for basic dyestuffs. In this respect it resembles Cachou de Laval and the benzidine series of direct colours.

CHAPTER XIV.

MUREXIDE. [17, 18, 19, 20.]

Murexide is the acid ammonium salt of purpuric acid, which does not exist in the free state. It is of historical interest, as besides picric acid it is the oldest artificial dyestuff used technically. Its application dates from the year 1853.

Murexide is obtained by action of ammonia on the mixture of alloxan and alloxantin, obtained by evaporating a solution of uric acid in strong nitric acid.

It is formed further by heating alloxantin in ammonia gas, and boiling uramil with mercuric oxide.

It forms four-sided prisms, with a green lustre, appearing red by transmitted light.

The composition of murexide is expressed by the formula $C_8H_4N_5O_6NH_4$. By double decomposition with potassium nitrate, the potassium salt ($C_8H_4N_5O_6K$) is obtained. The salts with calcium, barium, tin, and mercury are sparingly soluble red or violet precipitates.

Murexide dissolves in water with a fine purple-red colour, which is changed to blue-violet on addition of excess of alkali. Mineral acids set free purpuric acid, which immediately decomposes into uramil and alloxan, the solution being decolorised.

Murexide may be dyed on tin, lead, or mercury mordants, the last producing the best results. It is at present out of use.

CHAPTER XV.

DYESTUFFS OF UNKNOWN CONSTITUTION.

The following chapter comprises those dyestuffs which cannot be placed under the foregoing chemical classifications. It has already been mentioned that many of the dyestuffs treated of under the previous groups are of unknown constitution; but, being products of chemical synthesis, certain relationships to the various classes are easily deduced.

The number of colouring-matters included in the present chapter is unfortunately very large; most of them are natural products obtained from plant and animal sources. As these natural dyestuffs are very numerous, only those are described which are of interest from a technical or scientific point of view.

Although the artificial dyestuffs have to a great extent replaced the natural ones, certain of the latter still retain great importance in dyeing, being in fact indispensable, as no synthetical products have been able to do their work.

The great importance of a large number of the natural dyestuffs is based on the property which they possess of forming firmly-adherent lakes with metallic oxides. They are, like alizarin, adjective dyestuffs.

Some of them, for example Hæmatoxylin, Hæmateïn, Brasilin, and Brasileïn, are possibly quinones; others appear to be related to Euxanthone.

Some of these compounds are glucosides, which may be split up by action of dilute acids, forming a sugar, and a compound which is the real colouring-matter.

Some natural dyestuffs (Curcumin, Bixin, Carthamin) are capable, like the tetrazo dyestuffs, of dyeing on unmordanted cotton.

Hæmatoxylin [1, 2, 3, 13].

$C_{16}H_{14}O_6$.

Hæmatoxylin is contained in logwood or campeachy, the wood of *Hæmatoxylon campechianum.* Although scarcely a dyestuff, hæmatoxylin is the only important constituent of logwood, as on oxidation it yields hæmateïn [2], a compound of strong tinctorial properties.

Hæmatoxylin is prepared by extracting freshly rasped logwood with aqueous ether, evaporating, and mixing the residue with water [3]. The crystals which separate are recrystallised from water, preferably with addition of ammonium bisulphite to prevent oxidation.

Hæmatoxylin crystallises with $3\,H_2O$ in colourless tetragonal prisms [4], or with $1\,H_2O$ in rhombic crystals. It dissolves sparingly in cold water, and is dissolved with facility by hot water, alcohol, and ether. It has a sweet taste. It melts in its water of crystallisation somewhat over 100°. Its solution turns a ray of polarised light towards the right [3].

It dissolves in alkalies with a purple colour; the colour rapidly changes, with formation of hæmateïn, to blue-violet, afterwards becoming brown. Chromic acid, ferric chloride, and vanadic acid form higher oxidation products, which give black lakes with metallic oxides. On melting with potash, or on dry distillation, it yields pyrogallol and resorcin [99].

Formic acid has also been observed amongst the products formed in the potash melt [99].

Bromine acts on hæmatoxylin in acetic acid solution, forming a dibromo derivative. Acetic anhydride yields a pentacetyl derivative, $C_{16}H_9O_6(C_2H_3O)_5$, M.P. 165–166°, which on treating with bromine combines with four atoms, and by cautious bromination a monobromo derivative may be produced [6, 13, 99]. Nitrous and nitric acid convert hæmatoxylin to hæmateïn; the final product of oxidation with nitric acid is oxalic acid.

Hæmateïn [2, 3, 7].

$C_{16}H_{12}O_6$.

Hæmateïn is produced by careful oxidation of hæmatoxylin with nitric acid [5], or by action of atmospheric oxygen on an alkaline solution of this body [2, 3]. It is best obtained by exposing an ethereal hæmatoxylin solution mixed with a few drops of nitric acid to the air.

It forms dark green masses with a metallic lustre or lustrous silvery leaflets, which form a red powder on rubbing [5, 100]. It is sparingly soluble in hot water, alcohol, and ether, forming yellowish-brown solutions. Its alkaline solutions are bluish violet. The ammonia compound, $C_{16}H_{12}O_6,2NH_3$, is sparingly soluble and evolves ammonia on heating [3]. On treating with aqueous sulphurous acid, hæmateïn is dissolved without reduction, and forms easily soluble colourless addition compounds, which are decomposed on boiling. More stable compounds are obtained from hæmateïn and bisulphites.

Hæmateïn forms peculiar addition products with hydrochloric, hydrobromic, and sulphuric acids, which are decomposed by water at a high temperature [8].

In dyeing and printing, hæmatoxylin and hæmateïn are used in form of logwood extract or decoction.

Hæmatoxylin produces a greyish-violet shade on alumina mordants, probably due to formation of hæmateïn by oxidation. Copper salts produce a dark blue, iron salts and chromic acid a deep black. In practice, several of these mordants may be applied simultaneously; for example, logwood may be printed on an alumina mordant and afterwards passed through a bath of potassium bichromate or copper sulphate. The lakes with iron and chromium are derived from higher oxidation products which have as yet been little examined.

Logwood is largely used in cotton, wool, and silk dyeing. For wool, it serves especially for producing black on iron and chromium mordants. The wool is generally mordanted in a bath of bichromate and sulphuric acid and dyed in a logwood bath. Cotton is dyed black by alternate passages through logwood and bichromate baths. For production of a deep black without a violet tone, the addition of fustic or a similar yellow dyestuff is necessary. A mixture used in dyeing and printing, under the name of indigo substitute, is composed of logwood extract and chromium acetate.

Brazilin [1, 9, 10].

$C_{16}H_{14}O_5$.

Brazilin occurs in the wood of various species of *Cæsalpinia,* especially in *Cæsalpinia brasiliensis,* and with brazileïn forms the essential constituent of the dyewoods known as Brazil-wood, Peachwood, and Sapan-wood.

Brazilin often separates from the commercial extract of the dyewood in form of crystalline crusts [9], and these are the best material for a pure preparation of the compound. These crystals contain brazilin mixed with its calcium compound, and on boiling with very dilute alcohol, with a little hydrochloric acid and zinc powder, a solution is obtained from which brazilin crystallises on cooling.

Brazilin crystallises from water, according to the concentration of the solution, in clear amber rhombic crystals containing 1 H_2O, or in colourless needles [10] with $1\frac{1}{2}$ H_2O. It dissolves pretty easily in water, alcohol, and ether. Alkalies give a carmine-red solution, which is decolorised by zinc powder, the colour returning quickly on exposure to air. On dry distillation it gives large quantities of resorcin [9].

By action of nitric acid styphnic acid is formed; potassium chlorate and hydrochloric acid produce isotrichlorglyceric acid [12].

On adding lead acetate to an aqueous solution of brazilin, the lead compound separates in fine colourless needles, $C_{16}H_{12}PbO_5 + H_2O$, which rapidly turn red. On reduction with hydroiodic acid and phosphorus, brazilin yields brazinol, $C_{16}H_{14}O_4$, and finally $C_{16}H_{26}O_3$, both amorphous bodies [15]. On distillation with zinc powder, brazinol gives a hydrocarbon $C_{16}H_{14}$ or $C_{16}H_{16}$ [15].

Tetracetyl brazilin, $C_{16}H_{10}O_5(C_2H_3O)_4$ [11], and triacetyl brazilin are formed by treating brazilin with acetic anhydride [14].

Dibrom- and dichlorbrazilin are formed by cautious bromination and chlorination of brazilin [11, 13].

Brazilin is applied technically in form of extract or decoction of brazil-wood. It can be fixed only by use of mordants, and is used both in cotton and wool dyeing. On alumina mordants it produces shades resembling alizarin, but inferior both in beauty and fastness. The tin lake has a brighter colour. Wool mordanted with potassium bichromate is dyed a fine brown shade.

Brazileïn [11, 12, 7].

$C_{16}H_{12}O_5$.

Brazileïn bears the same relationship to brazilin that hæmateïn does to hæmatoxylin. It is formed by oxidation of an alkaline solution of brazilin in the air and by the action of alcoholic iodine solution [11] or of nitrous acid on the same compound.

Brazileïn forms grey silvery leaflets, which dissolve sparingly in water, easily in alkalies with a purple colour. Like hæmateïn, it forms unstable combinations with hydrochloric, hydrobromic, and sulphuric acids [8]. It resembles brazilin from a tinctorial point of view, but has greater dyeing power.

Morin [1, 16, 15].

$C_{12}H_{10}O_6 = C_{12}H_8O_5 + H_2O$.

Morin is the colouring-matter of fustic, the wood of *Morus tinctoria* (Jacq.) or *Macluria tinctoria* (Nettel). It is best prepared by boiling the wood with water and decomposing the lime compound with hydrochloric acid [17]. Morin crystallises from alcohol in long yellow needles. It is insoluble in water and carbon disulphide, sparingly soluble in ether, and easily in alcohol. It dissolves in alkalies with a dark yellow colour.

On dry distillation morin yields resorcin and paramorin. On treatment with sodium amalgam or by melting with caustic potash it yields phloroglucol, oxalic acid being also formed in the latter case [18].

Löwe ascribes to morin the formula $C_{15}H_{10}O_7 + 2H_2O$ [16].

It acts as a monobasic acid, the salts of the alkali metals are easily soluble, those with lime, aluminium, lead, and zinc almost insoluble [18].

Tribrommorin, $C_{12}H_7Br_3O_6$, is formed on treating morin with bromine [18].

Paramorin, $C_{12}H_8O_4$, formed by dry distillation of morin, forms yellow woolly crystals easily soluble in water, and which volatilise unchanged [19].

Isomorin [18] is formed by incomplete reduction of morin with sodium amalgam. It forms purple-red prisms, and yields morin on treatment with alkali or on heating. A compound known as maclurin or morintannic acid, $C_{13}H_{10}O_6$, is also contained in fustic, but is not a dyestuff.

Morin is used largely in wool and cotton dyeing as decoction or extract of fustic. Its principal application is in shading blacks, browns, &c. Wool is generally mordanted with potassium bichromate and sulphuric acid. The morin is fixed as a very stable chromium lake, which has a dull yellow colour.

Young fustic, the wood of *Rhus cotinus,* is totally different from old fustic. Koch isolated the colouring-matter [20], termed it fisetin, and gave it the formula $C_{15}H_{10}O_6$. This has been corrected by recent researches of Schmid [94]. According to this chemist, the colouring-matter of young fustic occurs as a glucoside in combination with tannic acid. This tannin compound splits up into the glucoside, fustin, $C_{46}H_{42}O_{21}$, and a tannic acid on warming with acetic acid. The glucoside splits up with dilute acids into sugar and fisetin, $C_{23}H_{10}O_3(OH)_6$. On boiling with acetic anhydride, hexacetyl fisetin, $C_{23}H_{10}O_9(C_2H_3O)_6$, M.P. 200°, is produced.

Hexamethyl fisetin, $C_{23}H_{10}O_9(CH_3)_6$, is formed by action of methyl iodide, M.P. 152° and 153°.

The principal use of fisetin is in wool-dyeing, especially for modifying cochineal scarlets.

Quercitrin [1, 21, 22, 24].

$$C_{36}H_{38}O_{20}+3H_2O.$$

Quercitrin is the colouring-matter of the dyewood known as quercitron bark, obtained from *Quercus tinctoria.*

Quercitrin may be obtained as follows:—The bark is boiled with strong alcohol and the extract precipitated with lead acetate and acetic acid. The filtrate is freed from lead by sulphuretted hydrogen, and evaporated. The residue is crystallised from water [25]. It forms light yellow lustrous needles, which contain one molecule H_2O after drying at 100°, and can be obtained anhydrous only by long heating at 130° [21]. It melts at 168° [22], dissolves sparingly in hot water, easily in alcohol. Its solution gives a green coloration with ferric chloride. Ammoniacal silver solution is reduced easily; Fehling's copper solution only after long boiling.

Quercitrin is a diabasic acid; the alkali salts are easily soluble, those with lead and alumina sparingly so. The former is easily soluble in dilute sulphuric acid.

Quercitrin is a glucoside; on boiling with dilute acids it yields isodulcite [24], $C_6H_{14}O_6$, and quercin, $C_{24}H_{16}O_{11}$. Quercitrin occurs also in hops, horse-chestnuts, tea, and many other plants. Tetrabromquercitrin is obtained by bromination in acetic acid solution and forms light yellow crystals [25].

Quercitin [24, 26, 27],

$C_{24}H_{16}O_{11}$,

is formed from quercitrin as above, according to the equation :

$$C_{36}H_{38}O_{20}+3H_2O=2C_6H_{14}O_6+C_{24}H_{16}O_{11} \quad [24].$$

It also occurs naturally in many plants.

It forms fine lemon-yellow needles, sparingly soluble in water, but readily in alcohol. It melts above 250°, and sublimes with partial decomposition. Its solution gives a green coloration with ferric chloride, which turns red on heating; lead acetate gives an orange precipitate. Silver nitrate is reduced in the cold, and Fehling's solution on warming. Nitric acid oxidises it to oxalic acid. On fusion with caustic potash, quercitin is split up, yielding querciglucin, $C_6H_6O_3$ (Phloroglucin?), and quercitic acid, $C_{15}H_{10}O_7$ [28].

At a higher temperature protocatechuic acid is formed. On reduction of quercitin the final product is phloroglucin [28].

Amide: by action of ammonia at 150°. Is a brown, amorphous compound. Dibromquercitin: light yellow needles. Diacetyldibromquercitin: yellow needles. Tetrabromquercitin: white needles. M.P. 218°.

Diacetyltetrabromquercitin: white needles, M.P. 226–228° [25].

Quercitin and quercitrin give beautiful yellow shades on cotton mordanted with alumina. With tin mordants a more orange shade is produced. On a large scale these bodies have an extensive application, and are used in form of a decoction of the bark or as flavin. In dyeing with the extract, it is probable that the quercitrin splits up, and that the shades obtained are due to the formation of quercitin lakes.

Flavin consists in some cases of nearly pure quercitrin and in others of quercitin. Quercitron and flavin serve principally for use with cochineal in dyeing scarlet. They are also used in calico-printing on iron, aluminium, and chromium mordants.

Rutin, the glucoside contained in Chinese yellow berries and in the leaves of *Ruta graveolens*, is closely allied to quercitrin. On boiling with dilute acids it splits up into quercitin and a sugar [29, 30, 31].

Xanthorhamnin, Rhamnetin [32, 33, 34].

These colouring-matters are contained in Persian berries, the fruit of *Rhamnus infectoria* and *oleoides*.

Xanthorhamnin (or Rhamnegin) is a glucoside of the composition $C_{48}H_{66}O_{29}$. It may be obtained by extracting the berries with alcohol. Resinous matters separate and are filtered off, and xanthorhamnin crystallises out afterwards. It may be purified by recrystallisation from alcohol [34]; the crystals obtained contain two molecules of alcohol, which are expelled at 120°. It is very easily soluble in water, less easily in alcohol, and insoluble in ether and chloroform.

It reduces silver nitrate and Fehling's copper solution. Its solution gives a dark brown coloration with ferric chloride, and a yellow precipitate with lead acetate and ammonia. On hydrolysis with dilute acids it gives rhamnetin and isodulcite; the same change may be effected by simply heating to 150°.

On acetylation with acetic anhydride (Schützenberger 33), twelve acetyl groups enter into xanthorhamnin.

Rhamnetin,

$C_{12}H_{10}O_5$ [34],

is formed along with isodulcite, $C_6H_{14}O_6$, by hydrolysis of xanthorhamnin. It forms a lemon-yellow powder sparingly soluble in water, alcohol, ether, and indifferent solvents. It is easily soluble in phenol, from which it crystallises in yellow needles. It reduces ammoniacal silver solution and Fehling's copper solution.

Its aqueous solution gives yellow or brownish-yellow precipitates with lead, alumina, barium, and lime-salts. On fusion with potash, or reduction with sodium amalgam, rhamnetin yields phloroglucin and protocatechuic acid.

Dimethylrhamnetin is formed by heating rhamnetin with potassium-methylsulphate, and methyl alcohol to 120°, M.P. 157° [34].

Herzig has recently found that the highest products obtained by methylation of rhamnetin and quercitin are identical, and has further obtained quercitin by removal of a methyl group from rhamnetin with hydriodic acid. From these results he regards rhamnetin as a dimethylquercitin.

Diacetylrhamnetin, M.P. 185° [34].

Dipropionylrhamnetin, M.P. 162° [34].

Dibenzoylrhamnetin, M.P. 210–212°.

These three compounds are obtained by action of the respective anhydrides on rhamnetin [34].

Dibromrhamnetin, obtained by bromination of rhamnetin in acetic acid solution, forms yellow needles soluble in hot benzene, alcohol, and acetic acid [34].

Diacetyldibromrhamnetin is formed by bromination of diacetylrhamnetin, M.P. 212° [34].

Xanthorhamnin is not a dyestuff, and it must therefore be accepted that rhamnetin is formed in the dyeing operations.

Rhamnetin in form of Persian-berry extract is of considerable importance in calico-printing; no artificial dyestuff has been found to replace it with advantage. It is generally fixed as tin or tin-alumina lake, both of which have a fine yellow colour. The chromium lake has a browner tone and is also used in printing. The alumina lake also sometimes used in dyeing has lemon shade; its principal application (mixed with chalk) is as an artists' colour.

Persian berries also contain rhamnin or β-rhamnegin, which yields β-rhamnetin on hydrolysis [39]. The composition of these bodies is unknown.

Luteolin [1, 36, 37, 38].

$C_{12}H_8O_5$.

Luteolin is the colouring-matter of weld, the leaves and skin of *Reseda luteola.* Luteolin crystallises from alcohol in small yellow needles which contain 1½ molecules of water of crystallisation, which are expelled at 150° [38]. It melts at 320° [36] and may be sublimed with partial decomposition. It is very sparingly soluble in water and ether; alcohol dissolves it with tolerable facility.

It dissolves readily in alkalies with a yellow colour, and gives yellow lakes with lead and alumina salts.

Ferric chloride produces a green coloration, changing to brown with excess of the reagent.

On fusion with potash, luteolin yields phloroglucin and photocatechuic acid [37].

Luteolin is obtained by extracting weld with dilute alcohol, evaporating the extract, and recrystallising the compound which separates.

An aqueous decoction of weld is used in dyeing. On alumina mordants it produces a beautiful fast yellow. Its principal application is in silk-dyeing, for which weld is a valuable material. Silk is previously mordanted with alum.

Bixin [48, 49, 50, 51],

$C_{28}H_{34}O_5$.

Bixin is the principal colouring-matter contained in annatto. This dyeware consists chiefly of the pulp of the fruit of *Bixa orellana* which has been allowed to ferment.

Bixin is prepared by boiling annatto with alcohol and sodium carbonate. On adding soda solution to the extract, the sodium compound of bixin separates; this is purified by recrystallising from dilute alcohol, and the bixin liberated by hydrochloric acid [51].

Bixin forms dark red metallic leaflets, M.P. 176°. It is almost insoluble in water, sparingly soluble in cold alcohol, benzene, glacial acetic acid, and ether, readily soluble in hot alcohol and in chloroform. Bixin is a dibasic acid. It reduces Fehling's solution in the cold. It forms a blue solution with concentrated sulphuric acid, which gives a dirty green precipitate on addition of water. Sodium amalgam converts it to a colourless compound, $C_{28}H_{40}O_5$ [51]. On oxidation with nitric acid, bixin yields oxalic acid. On distillation with zinc powder, it yields metaxylene, meta-ethyltoluene, and a hydrocarbon $C_{14}H_{14}$, ? [51].

Bixin gives two sodium salts: $NaC_{28}H_{33}O_5+H_2O$, forming coppery-red crystals, and $Na_2C_{28}H_{32}O_5$, a red powder [51].

Annatto contains a second colouring-matter known as Orellin, the composition of which is unknown. It dyes a yellow shade on alumina mordants, and is probably an oxidation product of bixin.

Bixin dyes both animal and vegetable fibres without a mordant. It is used both in silk and cotton dyeing in form of annatto. It is either fixed directly on cotton, or in form of its tin lake, the result being a fine orange-yellow shade. Annatto has a large application in colouring butter and cheese.

Chrysin [52],

$C_{15}H_{10}O_4$.

Chrysin occurs in the buds of the poplar (*Populus balsamifera* and *monilifera*). It forms light yellow needles, M.P. 275°, insoluble in water, sparingly soluble in benzene, ligroin, and cold alcohol, easily in glacial acetic acid, aniline, and hot alcohol. It dissolves in alkalies with a yellow colour. Its alcoholic solution is coloured dirty violet by ferric chloride, and gives a yellow precipitate with lead acetate. Chrysin is decomposed on boiling with concentrated potash solution, forming acetophenone, acetic acid, benzoic acid, and phloroglucin. On heating with methyl iodide it yields a monomethylether (tectochrysin), $C_{15}H_9O_3OCH_3$, which also occurs in poplar-buds. It forms thick sulphur-yellow crystals, M.P. 164°. It is insoluble in alkalies, sparingly soluble in alcohol, and easily in benzene.

Nitrochrysin, $C_{15}H_9NO_2O_4$, is formed by action of nitric acid on chrysin.

Dibromchrysin, $C_{15}H_8Br_2O_4$.

Diiodochrysin, $C_{15}H_8I_2O_4$.

Curcumin [53, 54, 55, 56].

$C_{14}H_{14}O_4$?

This slightly acid colouring-matter is contained in turmeric, the underground stem of *Curcuma longa* and *C. viridiflora*.

Curcumin is prepared by steaming turmeric, or extracting with carbon bisulphide to remove oily matters, and extracting the residue with ether. The crude product is purified by recrystallisation from ether or benzene. It forms orange-yellow prisms, M.P. 178° [56]. It is very sparingly soluble in hot water, more easily in benzene, and readily in alcohol, ether, and fatty oils. It dissolves in alkalies with a brown colour, and also gives a brown coloration with boric acid, changing to blue on addition of dilute alkali [53]. (Reaction for boric acid.) It gives insoluble brown lakes with lead calcium and barium salts. It dissolves in concentrated sulphuric acid with a cherry-red colour.

Nitric acid oxidises curcumin to oxalic acid; chromic acid produces terephthalic acid [54].

Curcumin is extensively used in dyeing, although not fast to light. Its principal application is in modifying red shades on cotton, for example saffranine. Curcumin dyes cotton without mordant. The powdered root is generally used suspended in water. The cotton is boiled in a mixture, and the curcumin becomes fixed as it dissolves. An alcoholic extract is sometimes used, and is mixed with water to an emulsion. Turmeric is also used for colouring butter, wax, and fatty oils.

Carotin [57, 58, 59],

$C_{18}H_{24}O$.

Carotin is the colouring-matter contained in the carrot (*Daucus carota*). It forms rhombic crystals, M.P. 168°, reddish brown in transmitted light, and gold green by reflected light. It is easily soluble in carbon disulphide, sparingly in alcohol and ether. It gives a violet solution with strong sulphuric acid, and is coloured blue by sulphurous acid. Arnaud [96] regards carotin as a hydrocarbon, but this assumption is extremely improbable from the properties of the compound.

Archil and Litmus.

Various kinds of lichens, for example *Lecanora tinctoria* and *Roccella tinctoria,* possess the property of giving violet or blue dyestuffs when submitted to the joint action of ammonia and air.

These lichens contain a number of peculiar acids (lecanoric acid, erythric acid, roccellic acid, &c.), which are split up by alkalies, the final products being orcin, $C_6H_3CH_3(OH)_2$, and erythrite, $C_4H_{10}O_4$.

Orcin is the only compound important for the production of lichen colours; with air and ammonia it yields orceïn, $C_7H_7NO_3$?, which is the principal dyestuff contained in archil [60, 61, 62, 63].

Orceïn gives sparingly soluble lakes with calcium and the heavy metals, but does not appear to be a real adjective dyestuff.

Commercial archil is prepared by moistening the weeds with ammonia and exposing the mixture to the air. Formerly putrid urine was used in place of the ammonia. The product obtained may be worked up into extract, "Archil liquor;" or dried and powdered, or is sold in the crude form as "Archil paste." These products all contain orceïn in form of its ammonia salt.

The dyeware known as Cudbear is similar to powdered archil. Besides orceïn, archil is said to contain two other colouring-matters of unknown composition, azoerythrin and erythroleic acid [60].

Archil is principally employed in wool and silk dyeing, less in calico-printing. It may be dyed on wool from acid, neutral, or alkaline baths. An addition of alum, stannous chloride, oxalic acid, or tartaric acid is made to the dyebath.

The calcium lake is used in printing, and is dissolved in acetic acid and fixed by steaming ("French purple"). The shades obtained with archil are purple, and may be modified with indigo or cochineal.

Archil has been displaced to a certain extent by azo dyestuffs, but still has considerable importance in wool-dyeing. This is due to the various conditions under which archil may be employed, and it can therefore be used to modify the shades of nearly all other dyestuffs.

Litmus.

If the lichens used for the manufacture of archil are submitted to a longer treatment with ammonia, potash and lime being also added, the orcin is converted to litmus—a dyestuff which is red in the free state, and yields blue salts. A similar product may be obtained direct from orcin by continued digestion with a mixture of ammonia and soda solution [64].

Litmus comes into commerce in small tablets mixed with chalk or gypsum, the commercial product containing only a small quantity of dyestuff.

Litmus is best known as an indicator in volumetric analysis, but is also used to inconsiderable extent for colouring wine and for blueing in laundries.

According to Kane (60), litmus contains four colouring-matters—Erythroleïn, Azolitmin, Erythrolitmin, and Spaniolitmin—the first two being the most important. It is improbable, however, that these compounds are chemical individuals.

According to Wartha (61), some kinds of litmus contain indigo.

Carthamin [62],

$C_{16}H_{17}O_7$ (?).

Safflower, the petals of *Carthamus tinctorius*, &c., contains, besides a yellow dyestuff, a red one, carthamine, which was of considerable importance before the introduction of the artificial dyestuffs.

To prepare carthamin, safflower is washed with water to remove the yellow dyestuff, and is then extracted with dilute soda solution, and filtered. Cotton yarn is immersed in the alkaline solution, and the liquid acidulated with citric acid. The cotton takes up the carthamin, which is removed with soda solution, and precipitated with citric acid. Obtained in this manner carthamin forms a lustrous green powder, sparingly soluble in water and ether, readily in alcohol. It dissolves in alkalies with yellowish-green colour. On fusion with potash it gives oxalic acid and para-oxybenzoic acid. Carthamin dyes animal fibres and unmordanted cotton from a slightly acid bath. It produces a beautiful pink colour on silk.

Carthamin enters commerce in a nearly pure state as safflower extract. For dyeing, the extract is dissolved in soda and the dyebath acidified with citric or other acid. In place of this extract the soda solution from safflower, which has been extracted with water, may be directly employed.

Carthamin is also used as rouge in admixture with talc, chalk, or starch. It is also employed as an artists' colour.

The yellow colouring-matter of safflower, which according to Malin has the composition $C_{24}H_{30}O_{15}$ [63], is of no importance in dyeing.

Santalin [64, 65, 66].

Sandal-wood or Sanders-wood (from *Pterocarpus santalinus*) contains a resinous red dyestuff of slightly acid properties. Santalin, $C_{15}H_{14}O_5$, is obtained by precipitating an alcoholic extract of sandal-wood with lead acetate, and decomposing the lead lake with dilute sulphuric acid. It crystallises from alcohol in red prisms, M.P. 104°. It is sparingly soluble in water, dissolves in alcohol and ether with a blood-red colour, and in alkalies with a violet colour. It gives violet insoluble lakes with calcium, barium, and the heavy metals.

Franchimont [67], who could obtain santalin only in an amorphous state, ascribes to it the formula $C_{17}H_{16}O_6$. On heating with hydrochloric acid to 200°, he obtained methyl chloride and an amorphous body ($C_8H_{19}O_5$?), which gives a violet-black solution with alkalies.

Santalin is largely used in wool-dyeing and is employed as rasped sanders-wood, which is directly added to the dyebath. It produces a good reddish-brown shade on chromed wool, which is, however, not very fast to light.

An alcoholic extract of sanders-wood is also used for colouring tinctures, varnishes, and also for staining wood.

Alkannin [70],

$C_{15}H_{14}O_4$.

Alkanet, the root of *Anchusa tinctoria*, contains the above red dyestuff. It is of slightly acid character, and has not been obtained in a crystalline state. It is insoluble in water, dissolves easily in alcohol, ether, ligroin, and fatty oils, forming red solutions. It dissolves in alkalies with a blue colour, and is reprecipitated by acids in red flakes. It gives an insoluble lake with baryta. It is probably a derivative of methylanthracene, $C_{15}H_{12}$, as it yields this hydrocarbon on distillation with zinc powder [93].

The diacetyl compound, $C_{15}H_{12}(C_2H_3O)_2O_4$, is formed by the action of acetic anhydride and sodium acetate [70].

Alkannin dissolves in concentrated sulphuric acid with a blue colour. Nitric acid oxidises it to oxalic acid and succinic acid.

Alkannin (in form of an extract of alkanet root) is used for colouring oils, pomades, tinctures, &c.

Crocin and Crocetin.

Saffron, the stigmata of *Crocus sativus*, contains according to Quadrat [71] and Weiss [72] a yellow glucoside, polychroite, $C_{48}H_{68}O_{18}$ [73]. According to these chemists it may be split up into crocin, $C_{16}H_{18}O_6$, sugar, and an ethereal oil.

R. Kayser [74] terms polychroit "crocin," and crocin "crocetin," and ascribes to the former the formula $C_{44}H_{70}O_{28}$, and to the latter $C_{34}H_{46}O_9$. According to him, crocin splits up into crocetin and saffron sugar, $C_6H_{12}O_6$, while the ethereal oil is a product of the decomposition of picrocrocin.

L. Meyer [73] and Rochleder obtained crocin from the pods of *Gardenia grandiflora*, but it is not certain whether their product is identical with the above. They obtained a glucoside, $C_{58}H_{86}O_{31}$, which splits up into sugar and crocetin, $C_{34}H_{36}O_4$. As these bodies were only obtained in an amorphous state, these formulæ appear to be doubtful.

Lo-Kao (CHINESE GREEN).

The above is a commercial green dyestuff prepared from the bark of various species of Rhamnus (*Rhamnus utilis, Rh. chlorophlorus*). It consists chiefly of the alumina and lime lakes of the glucoside.

This latter is termed lokaïn by Cloëz and Guignet [75], and lokaonic acid by Kayser [76].

According to Cloëz and Guignet a compound has the formula $C_{28}H_{34}O_{17}$, and is decomposed by acids, yielding glucose and lokaëtin, $C_9H_8O_5$ [75]. Kayser, on the other hand, gives to lokaïn (lokaonic acid) the formula $C_{42}H_{48}O_{27}$, and to lokaëtin (lokanic acid) the formula $C_{36}H_{36}O_{21}$. The sugar produced in the formation of the latter is not glucose, but an inactive modification which Kayser terms Lokaose. Lokaïn forms a deep bluish-black mass which takes a metallic lustre on rubbing. It is insoluble in water, alcohol, ether, chloroform, and benzene, but soluble in alkalies with a blue colour, which is changed to red by reducing agents.

The ammonium salt forms lustrous bronzy crystals. The other salts are amorphous; those of the heavy metals are insoluble.

Lokaëtin (lokanic acid) forms a violet-black powder only soluble in alkalies, with a violet colour.

According to Kayser it reacts with sulphuretted hydrogen, forming a crystalline compound containing sulphur.

Concentrated sulphuric acid produces a brown amorphous compound, which is stated to be $C_7H_6O_4$ by Cloëz and Guignet, and $C_{36}H_{26}O_{16}$ by Kayser.

The formulæ for the compounds described above must be regarded as doubtful, as the nature of the substances affords little guarantee for their purity, and the analysis gives little idea of the true size of the molecules.

Lo-kao is used, especially by the Chinese, for dyeing wool and silk. It may be fixed on cotton from an alkaline bath, but is also frequently used in a reduced state as a vat, stannous chloride or ammonium sulphide being used as reducing agents. The shade produced is a fine bluish green, very fast to light.

Cochineal.

The important dyeware known as cochineal consists of the dried female of an insect, the *Coccus cacti coccinellifera*, which lives on certain species of cactus. The colouring principle of cochineal is glucoside carminic acid, of the formula $C_{17}H_{16}O_{10}$ [77].

Carminic acid is prepared by precipitating an aqueous decoction of cochineal with lead acetate, and decomposing the lead lake with a quantity of sulphuric acid insufficient for the whole. The solution of carminic acid thus obtained is evaporated to dryness at a low temperature, and the residue crystallised from absolute alcohol.

Obtained in this manner, carminic acid forms a purple-brown mass which gives a scarlet powder on trituration. It is with difficulty soluble in ether, easily in water and alcohol.

It is a weak dibasic acid, forming violet salts; those with the alkalies are easily soluble, with the earths and heavy metals they are insoluble. The sodium salt may be crystallised; the other salts are amorphous.

On boiling with dilute acids, carminic acid is split up into carmine-red, $C_{11}H_{12}O_7$, and a sugar, $C_6H_{10}O_5$. In general, carminic acid gives the same decomposition products as carmine-red. If an ammoniacal solution is allowed to stand, a nitrogenous compound is formed, possessing totally different dyeing properties. On a large scale this product is prepared for dyeing by maceration of ground cochineal with ammonia, and is used under the name of ammoniacal cochineal.

In dyeing, this product gives much bluer shades, and is used for modifying cochineal scarlets.

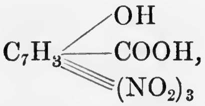
Carmine-red.

$C_{11}H_{12}O_7$.

Carmine-red is prepared from the lake obtained by precipitating a cochineal decoction with lead acetate. This lead lake is dissolved in dilute sulphuric acid, freed from lead by sulphuretted hydrogen, and boiled with very dilute sulphuric acid for some hours. Barium carbonate is added till a violet coloration ensues, and then filtered rapidly and precipitated with lead acetate. The lead lake is decomposed and the filtrate evaporated to dryness *in vacuo*.

Carmine-red is a dark red substance, which appears green by reflected light. It is insoluble in ether, but soluble in water and alcohol with a red colour. Reducing agents convert it to a colourless compound. On fusion with potash carminic acid yields coccinin [80], and on heating with water to 200° ruficarmine is formed [82].

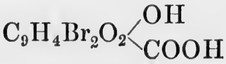
By boiling carminic acid with nitric acid, trinitrococcussic acid (trinitrocresotinic acid),



$$C_7H_3\begin{cases}OH\\COOH,\\(NO_2)_3\end{cases}$$

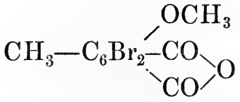
is formed [78].

Bromine reacts with carminic acid, producing two brominated compounds. α-bromcarmine, $C_{10}H_4Br_4O_3$ [81], forms colourless needles, M.P. 248°, which are soluble in alkalies. On boiling with strong potash solution it yields oxybromcarmine, which behaves like an oxyacid of the formula



$$C_9H_4Br_2O_2\begin{cases}OH\\COOH\end{cases}$$ [81].

On oxidation with potassium permanganate, oxybromcarmine yields an acid of the formula $C_9H_6Br_2O_4$, probably dibromoxytolylformic acid, $C_7H_5OBr_2COCOOH$. Dibrommethoxylmethylphthalic anhydride,

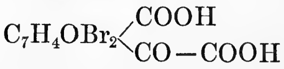


$$CH_3-C_6Br_2\begin{array}{l}\diagup OCH_3\\ -CO\diagdown\\ \diagdown CO\diagup\end{array}O$$

is also formed [81].

β-bromcarmine, $C_{11}H_5Br_3O_4$, forms yellow needles, M.P. 232°, and gives red dibasic salts with the alkalies.

On oxidation with potassium permanganate it yields dibromoxymethylbenzoyldicarbonic acid,



$$C_7H_4OBr_2\begin{array}{l}\diagup COOH\\ \diagdown CO-COOH\end{array}$$

and the above dibrommethoxymethylphthalic anhydride [81].

Ruficoccin, $C_{16}H_{10}O_6$, is formed along with a compound of the composition $C_{32}H_{20}O_{13}$ by heating carmine-red with sulphuric acid to 130–140° [82].

Ruficoccin is a brick-red powder, sparingly soluble in water and ether, easily soluble in alcohol. It dissolves in alkalies with a brown colour. On distillation with zinc powder a hydrocarbon, $C_{16}H_{12}$, is formed [82].

Ruficarmine [82] forms a carmine-red powder insoluble in water, but easily soluble in alcohol.

Carmine-red is a dibasic acid, and forms salts similar to those of carminic acid.

Coccinin, $C_{14}H_{12}O_5$ [80], is formed on melting carminic acid or carmine-red with potash. It forms yellow leaflets, insoluble in water, but soluble in alcohol and alkalies. The alkaline solution becomes oxidised on exposure to the air, the colour changing through green to red. A solution of coccinin in concentrated sulphuric acid gives a blue coloration on addition of manganese dioxide.

Carmine.—This is a commercial product made from cochineal, which is used by artists and for colouring confectionery, and also as rouge. Carmine forms porous red masses, which are easily rubbed to fine powder. It is insoluble in water and alcohol, but dissolves completely in ammonia if free from adulteration with kaolin, starch, &c.

The exact method employed for this preparation is unknown; various recipes are in vogue, according to which the essential consists in precipitating an aqueous decoction of cochineal with alum. According to the researches of Liebermann [83] carmine contains about 3 per cent. of alumina and about the same quantity of lime, and also about 20 per cent. of albuminoid matters.

As the lime and alumina dissolve in ammonia and cannot be detected therein by the ordinary reagents, it is probable that a peculiar lake of carmine-red is present, in which the albuminoids play a part.

The colour of carmine, and especially that of its ammoniacal solution, differ considerably from that of carmine-red.

The above ammoniacal solutions were formerly used as red ink.

Cochineal is employed in dyeing for production of scarlet shades. Before the introduction of the red azo-dyestuffs cochineal was the only material which could be used for scarlets, but recently, owing to competition with the artificial dyestuffs, its use has greatly diminished. Neither carminic acid nor carmine-red can be fixed without mordant. The finest scarlet tones are obtained with the tin lake of carminic acid, or probably of the carmine-red formed by its decomposition.

In dyeing wool scarlet, the mordanting and dyeing operations are generally carried out in one bath, the material being boiled with ground cochineal and stannous chloride, an addition of tartar or oxalic acid being generally made. Yellower shades are obtained by addition of weld, flavine, or fustic.

The alumina lake has violet colour, and the iron a blackish-grey. Owing to the latter, it is important to have water mordants, &c., perfectly free from iron in dyeing cochineal scarlet.

Ammoniacal cochineal produces bluer shades on tin mordants. Cochineal is seldom used in cotton-dyeing. Cochineal lakes are often used in printing, being mixed with albumen and fixed by steaming. The artists' colour known as Florentine lake is prepared by precipitating a decoction of cochineal with alum and soda or chalk. It contains the alumina lake of carminic acid, mixed with excess of alumina and chalk.

Lac-dye.

Lac-dye is also a product of a species of *Coccus*, the *Coccus lacca* or *C. ficus*. These insects live on the branches of *Ficus religiosa* and *Ficus indica*. A resinous matter exudes from the tree and envelopes the insects. The twigs are cut off along with the resin, and sold as stick-lac. On treating stick-lac with water, the colouring-matter dissolves, and the residue, melted and squeezed through calico, forms commercial shellac. The exact method by which commercial lac-dye is prepared is kept secret, but it probably consists in precipitation of an alkaline decoction of stick-lac with alum.

The colouring-matter contained in lac-dye was long considered to be identical with that of cochineal, but, as shown by the researches of R. E. Schmidt [95], it is a new body, laccainic acid, $C_{16}H_{12}O_8$.

Lac-dye is used in dyeing in a similar manner to cochineal, the principal difference being that it requires a very acid bath. The shades produced are not so clear as those of cochineal, but surpass the latter in fastness both to light and alkalies.

Kermes, another insect (*Coccus ilicis, C. baphia*), contains analogous colouring-matters, and was formerly used in dyeing, but has now gone out of use.

Other insects, for example *Coccus polonicus, C. fragariæ*, contain red dyestuffs.

Colouring-matter of Tyrian Purple [84, 85].

Certain molluscs (*Purpura lapillus, P. hæmastoma*, and various species of *Murex*), when crushed and exposed to sunlight, develop a purple dyestuff which was highly prized by the ancients. According to Schunck [84] the dyestuff, punicine, is insoluble in water, alcohol, and ether, slightly soluble in benzene and glacial acetic acid, and easily soluble in aniline and concentrated sulphuric acid [85]. It sublimes with partial decomposition in leaflets, which have a metallic lustre.

Witt regards this dyestuff as indigo mixed with a red dyestuff less fast to light. On ancient purple cloth this red has been bleached in course of time, and only the blue-indigo ground remains. Compare Witt [98].

Catechu.

The commercial products known as Catechu and Cutch are prepared by evaporation of aqueous extracts of the wood of *Acacia catechu* and allied species, common in India. Gambier is a similar preparation; its exact composition has not been investigated. Catechu serves technically both as a colouring-matter and as a tannin, and is largely employed in cotton-dyeing and in tanning.

The principal constituents of catechu are catechin and catechu-tannic acid.

Catechin.—On treating catechu with cold water, catechu-tannic acid dissolves, and the catechin contained in the residues may be obtained by extraction with boiling-water. Catechin separates from the solution on cooling, and may be purified by recrystallising from boiling-water. It forms minute white needles, M.P. 217°, which are sparingly soluble in cold water, readily in alcohol and in boiling-water. Catechin yields pyrocatechin and phloroglucin on heating with dilute sulphuric acid under pressure. It does not precipitate solutions of gelatine, tartar-emetic, or alkaloids, thus differing from the tannins.

There is some uncertainty as to the exact composition of catechin. Liebermann and Tauchert give the formula

$$C_{21}H_{20}O_9 + 5H_2O$$

as most probable, and they have also analysed a diacetyl compound, M.P. 128°–130°, which supports this formula [105].

Etti ascribes to catechin the formula $C_{38}H_{36}O_{16}$, and uses this in the following series of anhydrides described by him [106].

By the action of heat, or of dilute acids, catechin gives rise to a series of anhydrides. The first of these, catechu-tannic acid, $C_{38}H_{34}O_{15}$, is a natural constituent of catechu. This compound, and the dianhydride $C_{38}H_{32}O_{14}$, and the trianhydride $C_{38}H_{30}O_{13}$, precipitate gelatine, and have a resemblance to the true tannins. Further heating gives rise to the production of a fourth anhydride, catechuretin, $C_{38}H_{28}O_{12}$, a compound insoluble in water.

Catechin reacts with two molecules of diazobenzene chloride, producing a catechinazobenzene.

On oxidation with potassium bichromate, catechin yields japonic acid, a reddish-brown compound, the chromium or copper lake of which is probably formed in the ordinary methods of dyeing with catechu.

Catechu-tannic Acid.—This body, also known as catechin-red, is obtained by extracting catechu with cold water, or by heating catechin with water to 110°. It precipitates gelatine but not tartar-emetic, and gives a green coloration with ferric acetate.

It yields a reddish-brown compound on oxidation with potassium bichromate, probably identical with the japonic acid formed on oxidation of catechin.

Catechu is principally used in cotton-dyeing. It gives yellowish shades on goods mordanted with aluminium or tin salts; but its main application is for the production of brown shades, which are very fast. The goods are steeped in a solution of catechu and passed through a bath of potassium bichromate, to which copper sulphate is sometimes added. The brown may also be developed by airing or ageing. In calico-printing, catechu may be fixed by one of the methods used for aniline black. A mixture of catechu, potassium chlorate, and sal-ammoniac is printed, and the colour developed by steaming.

Cachou de Laval [97].

The above dyestuff, also known as Fast Grey, is a commercial product prepared by melting various organic substances (sawdust, bran, &c.) with sodium sulphide.

These products, discovered by Croissant and Bretonnière, contain peculiar weak acid dyestuffs, which contain sulphur.

Cachou de Laval dyes unmordanted cotton from an alkaline bath, producing brownish shades, which are capable of modification by passage through baths of various metallic salts (copper and iron, chromium salts). In spite of its very unpleasant smell, it has an extensive application in cotton-dyeing.

The shades are very fast to soap. Like canarin and the direct dyeing tetrazo-colours, Cachou de Laval is capable of fixing basic dyestuffs, and the shades can thus be topped at will.

By fusing sodium acetate with sulphur, E. Kopp obtained a substance closely resembling Cachou de Laval in its properties.

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The references are divided into the following sections :—

1. INTRODUCTION.
2. NITRO-COMPOUNDS.
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4. OXYQUINONES AND QUINONEOXIMES.
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7. QUINONEIMIDE AND AZINE DYESTUFFS.
8. ANILINE BLACK, INDULINES AND NIGROSINES.
9. QUINOLINE AND ACRIDINE DYESTUFFS.
10. INDIGO DYESTUFFS.
11. EUXANTHIC ACID, GALLOFLAVINE, CANARINE, AND MUREXIDE.
12. DYESTUFFS OF UNKNOWN CONSTITUTION.

ABBREVIATIONS.

Ber. = Berichte der deutschen chemischen Gesellschaft zu Berlin.

Annal. = Annalen d. Chemie und Pharmazie (now Liebig's Annalen).

Journ. f. pr. Chem. = Journal für practische Chemie.

Jahresb. = Jahresbericht über die Fortschritte d. Chemie (Giessen: Ricker, publisher).

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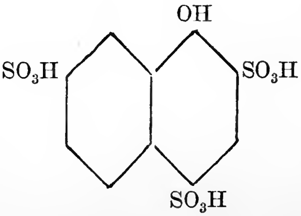
APPENDIX.

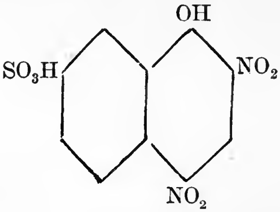
NITRO-COMPOUNDS.

P. 25. *Naphthol Yellow S.*

The *α*-naphtholtrisulphonic acid used in the manufacture of naphthol yellow S has the constitutional formula :



The free acid of naphthol yellow S is constituted according to the formula :



AZO-DYES.

P. 56. *Chromotropes.*

These colouring-matters are prepared by action of diazo-compounds on the chromotrope acid (see p. 295). The commercial brands are 2 R, 2 B, 6 B, 8 B, and 10 B. They dye wool from an acid bath; the shades vary from a bright scarlet with 2 R to a reddish violet with 10 B, but are not fast to soap. More valuable results are obtained when the chromotropes are applied in conjunction with a mordant. Darker and faster shades are obtained by boiling the goods dyed with these dyestuffs with salts of copper, aluminium, and iron, and various shades of black are produced by action of potassium bichromate. It has been found advantageous to use the mordant after dyeing, the operation taking place in the same bath. Chromotrope 8 B gives the best and fastest shade of black. The property of combining with metallic mordants possessed by these dyestuffs is due to the presence of two hydroxyl-groups in the peri position. Chromotropes 2 R, 2 B, and 6 B give a red solution with concentrated sulphuric acid, 8 B and 10 B give a blue solution.

Amidonaphtholsulphonic Acids.

Several of these acids are known, but only one, the γ or G acid, is of importance. It is prepared by action of caustic soda on β-naphthylaminedisulphonic acid G (from β-naphtholdisulphonic acid and ammonia) at about 260°. It may be diazotised, and reacts with diazo-compounds to produce azo-colours, which may be diazotised and combined on the fibre with other amines and phenols. (See below, under Tetrazo-colours.)

The reaction between tetrazo-compounds and γ-amidonaphtholsulphonic acid may be effected in either alkaline or slightly acid solution, and the products differ according to which condition is observed. The exact reason for this behaviour has not been explained. For example, in the preparation of diamine blacks R and B, and diamine blue-black E, the combination of the tetrazo-compound with γ-amidonaphtholsulphonic acid is effected in alkaline solution, while in the cases of Diamine Violet and Fast Red a slightly acid solution is used.

P. 60. The following Azo-dyes contain the groups necessary theoretically for the formation of mordant-dyeing colours. In fact they yield fast shades when applied in conjunction with a chromium mordant. It may be remarked that Diamond Black (p. 66) belongs to the same category.

Dyestuff.	*Diazotised Base.*	*Combined with*
Diamond Yellow G..	M-amidobenzoic acid.	Salicylic acid.
Diamond Yellow R..	O-amidobenzoic acid.	Salicylic acid.
Cloth Brown R	Benzidine.	1 mol. salicylic acid, 1 mol. α-naphtholsulphonic acid.
Cloth Brown G	"	1 mol. salicylic acid, 1 mol. ββ-dioxynaphthalene.
Cloth Orange	"	1 mol. salicylic acid, 1 mol. resorcin.

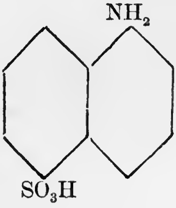
P. 66. Several black dyes of the disazo class have recently appeared in commerce, and the more important of these are given here. In the list the diazo-compound of the first-named body is allowed to react with the second, and the resulting amido-azo-compound is diazotised and combined with the third constituent.

Blue-Black B .... *Azo Black*	β-naphthylaminesulphonic acid + α-naphthylamine + β-naphtholdisulphonic acid R.
Naphthol Black B	β-naphthylamine-γ-disulphonic acid + α-naphthylamine + R acid.
Naphthol Black 3 *B* ..	α-naphthylaminedisulphonic acid B + α-naphthylamine + R acid.
Naphthol Black 6 *B*..	α-naphthylaminedisulphonic acid (Dahl) + α-naphthylamine + R acid.
New Black .... *Anthracite Black*	α-naphthylaminedisulphonic acid B + α-naphthylamine + diphenylmetaphenylenediamine.
Victoria Black	Sulphanilic acid + α-naphthylamine + 1·8 dioxynaphthalenesulphonic acid.

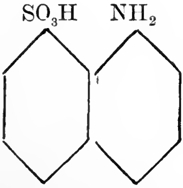
P. 69. *α-Naphthylaminesulphonic Acids.*

On nitration of α-naphthalene-sulphonic acid, or on sulphonation of α-nitronaphthalene, a mixture of two acids is formed. These are separated by taking advantage of the different solubilities of their sodium salts in water.

The sparingly soluble sodium salt yields an α-naphthylaminesulphonic acid on reduction, which has the constitution expressed by the formula:



It is known as naphthalidinesulphonic acid or simply as Laurent's acid. It is used, but not to any great extent, in the manufacture of azo-colours. The more easily soluble sodium salt obtained above yields *a*-naphthylaminesulphonic acid S (peri-acid) on reduction. It has the constitution :



It has hitherto not been made use of in the preparation of azo-dyes.

The preparation of these acids is described in British Patents Nos. 15775 and 15782, 1885.

The Laurent acid is also formed by action of fuming sulphuric acid on *a*-naphthylamine hydrochloride or on acet-*a*-naphthalide.

a-Naphthylaminedisulphonic Acids.

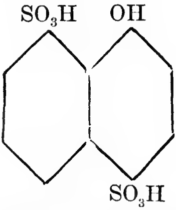
Certain of these acids are used in the manufacture of black azo-colours. A mixture of acids is formed by sulphonation of naphthionic acid with fuming sulphuric acid, and these are separated by treating the calcium salts of the mixture with alcohol. The calcium salt soluble in alcohol of 96 °/ₒ yields acid No. I., the residue contains acids II. and III., of which II. is soluble in alcohol of 85 °/ₒ. Acid I. yields azo-colours of no value, and No. III. is of greater importance than No. II. Germ. Pat. 41957, Sept. 4, 1886.

β-Naphthylaminedisulphonic Acids.

These acids are prepared by heating the corresponding *β*-naphtholdisulphonic acids with ammonia. Thus R acid yields R-amido-acid and G-(*γ*)-acid yields G-(*γ*)-amido-acid. The G-amido-acid is also obtained by sulphonation of *β*-naphthylamine at 100–140° with fuming sulphuric acid.

a-Naphtholdisulphonic Acids.

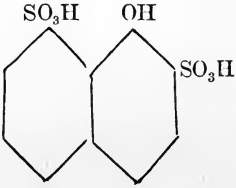
I. *Schöllkopf acid.*—*a*-naphthylaminesulphonic acid S (*suprà*) is sulphonated, and the resulting disulphonic acid converted into naphtholdisulphonic acid by the diazo-reaction. The Schöllkopf acid has the constitution



(Brit. P. 1885, 15775–15782). It is used in the manufacture of azo-dyes.

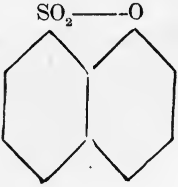
II. *a-naphthol-ε-disulphonic acid* (Andresen acid).—The mixture of disulphonic acids obtained by sulphonation of naphthalene is nitrated and reduced. The sodium salts of the amidodisulphonic acids obtained are treated with water. The more easily soluble salt yields the Andresen acid by the diazo-reaction, the sparingly soluble one corresponds to the Schöllkopf acid.

The Andresen acid has the constitution

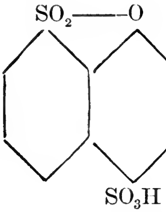


It yields azo-dyes of a pure bluish shade, and is, next to the Nevile-Winther acid, the most important derivative of *α*-naphthol.

A peculiar property possessed by *α*-naphtholsulphonic acids which contain hydroxyl- and sulpho-groups in the peri (1·8) position, is that they yield anhydrides by elimination of water, and these anhydrides (called sultones) are frequently obtained in place of the acids, on decomposing the diazo-compounds with boiling water. Thus the naphtholsulphonic acid corresponding to *a*-naphthylaminesulphonic acid S yields naphtho-sultone,



The Schöllkopf acid gives naphthosultone-sulphonic acid,

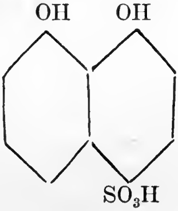


while an isomer is obtained from the Andresen acid. (Literature: G. Schultz, Ber. xx. p. 3162; H. Erdmann, Annalen, ccxlvii. p. 344; Bernsthen, Ber. xxii. p. 3327; Armstrong & Wynne, Proc. Chem. Soc. 1890, p. 125. Brit. Patents, 1885, 15775–15782; 1888, 4625, 5910.)

Dioxynaphthalenesulphonic Acids.

Several of these acids are used in the manufacture of azo-colours.

I. Dioxynaphthalenemonosulphonic acid S is prepared by melting *a*-naphtholdisulphonic acid (Schöllkopf) with caustic soda, and has accordingly the constitutional formula:



Azo-fuchsine B. Diazotoluene and dioxynaphthalenesulphonic Acid S.

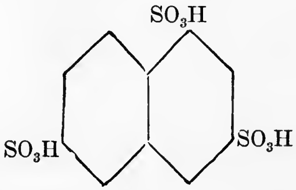
Azo-fuchsine G. Diazobenzenesulphonic acid and dioxynaphthalenesulphonic Acid S.

These two dyestuffs dissolve in water with a bluish-red colour, and in concentrated sulphuric acid with a violet colour. Azo-fuchsine B comes into commerce as a brownish-black powder, azo-fuchsine G as a reddish-brown powder.

They produce magenta shades on wool and are recommended as substitutes for acid magenta on account of their fastness to light and the clearness of the shades obtained. They may also be used for printing woollens prepared with alum and stannic chloride. German Pat. 54116, Oct. 25, 1889.

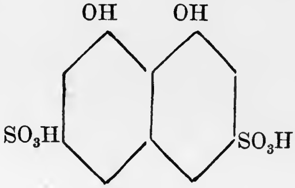
Dioxynaphthalenedisulphonic Acid (Chromotrope Acid).

Naphthalene is sulphonated with fuming sulphuric acid at from 80°–180° according to the strength of acid employed. The trisulphonic acid obtained has the constitution



It is nitrated and reduced, and the resulting amido-acid submitted to the diazo-reaction whereby *a*-naphtholtrisulphonic acid or its sultone is formed. This yields a dioxynaphthalenedisulphonic acid (Chromotrope Acid) on fusion with caustic soda.

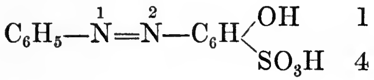
The chromotrope acid is constituted according to the formula:



Dyes from Benzidine and Analogous Bases.

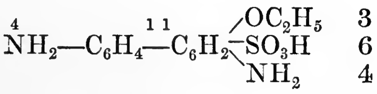
In the Table on p. 72 several derivatives of ethoxybenzidine are enumerated, and the reactions whereby this base is obtained are described here. Diazobenzene chloride reacts with *p*-phenolsulphonic acid, producing benzene-azo-paraphenolsulphonic acid, the azo-chain taking up an ortho-position with regard to the hydroxyl-group.

Accordingly the compound is constituted according to the formula:



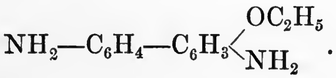
$$C_6H_5-\overset{1}{N}=\overset{2}{N}-C_6H\left\langle\begin{array}{ll}OH & 1\\ SO_3H & 4\end{array}\right.$$

On heating with ethyl chloride or bromide and alcohol in presence of alcoholic potash, an ether is formed. On reduction with stannous chloride or zinc-powder and caustic soda, the ether undergoes an intramolecular change, a sulphonic acid of ethoxybenzidine, of the constitution:



$$\overset{4}{N}H_2-C_6H_{\overset{1}{4}}-\overset{1}{C_6}H_2\left\langle\begin{array}{ll}OC_2H_5 & 3\\ SO_3H & 6\\ NH_2 & 4\end{array}\right.$$

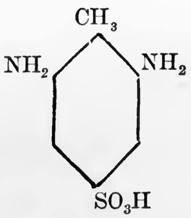
is formed. This is heated with water under pressure to 170°, and sulphuric acid splits off, forming ethoxybenzidine sulphate.



$$NH_2-C_6H_4-C_6H_3\left\langle\begin{array}{l}OC_2H_5\\ NH_2\end{array}\right. .$$

Ethoxybenzidine is used in the manufacture of a number of the so-called diamine colours.

Toluylenediaminesulphonic acid of the constitution



may be diazotised. The tetrazo-compound reacts with amines and phenols; the toluylene browns are combinations with two molecules of a metadiamine.

In the Table on p. 74, cotton-yellow and salmon-red are erroneously described as obtained from diamidodiphenylene. They are derivatives of diamidodiphenylurea, but are prepared indirectly.

Cotton-yellow is obtained by action of phosgene on two molecules of amidobenzene-azo-salicylic acid, and has the formula:

$$CO[NH-C_6H_4-N=N-C_6H_3.OH.COOH]_2.$$

Salmon-red is prepared in an analogous manner from amidobenzene-azonaphthionic acid, and has the formula:

$$CO[NH-C_6H_4-N=N-C_{10}H_5NH_2.SO_3H]_2.$$

Mimosa is prepared by action of ammonia on the diazo-compound of primuline.

Mikado Colours.—The yellow-orange and brown dyestuffs known under this designation are prepared by action of alkalies on paranitrotoluenesulphonic acid in presence of oxidizable substances, such as arsenious acid, glycerine, phenols, tannic acids, &c. Brit. Pat. 1888, 2664.

They are probably more or less impure azoxystilbenedisulphonic acids. They dye cotton directly from a salt bath and give moderately fast shades.

The following Table comprises some of the most important direct dyes of recent introduction.

Dyestuff.	*Diazotised Base.*	*Combined with*
Toluylene Orange....	Benzidine.	1 mol. toluylene-diamine-sulphonic acid. 1 mol. O-cresol-carbonic acid.
Diamine Scarlet	„	2 mols. β-naphthol γ-disulphonic acid. 1 mol. phenol.
Diamine Scarlet R ..	„	1 mol. β-naphthol G-disulphonic acid. The product is ethylated.
Diamine Brown V ..	„	1 mol. γ-amidonaphthol-sulphonic acid. 1 mol. m-phenylenediamine.
Thiazol Yellow Clayton Yellow	Dehydrothio toluidine-sulphonic acid.	Dehydrothiotoluidinesulphonic acid.

Congo Brown G & R are prepared by action of diazotised sulphanilic acid and naphthionic acid respectively on the combination obtained from tetrazo-diphenyl with 1 mol. of salicylic acid and 1 mol. of resorcin.

Diamine Blue 6 *G.*—β-naphthylaminedisulphonic acid diazotised and combined with 1·2 amidonaphthol ether. The product is diazotised and combined with β-naphthol.

Benzo-grey.—Tetrazodiphenyl is combined with equal molecules of salicylic acid and α-naphthylamine, the product diazotised and combined with α-naphtholsulphonic acid (Nevile and Winther).

Benzo-olive.—Is prepared similarly to the above; dioxynaphthalenesulphonic acid S being substituted for the last-named component.

Benzo-indigo-blue.—The combination of benzidine with 1 mol. α-naphthylamine is diazotised and combined with two molecules of dioxynaphthalenesulphonic acid S.

OXYQUINONES AND QUINONE OXIMES.

P. 91. *Alizarin-blue S* has the composition expressed by the formula:

$$C_{17}H_9NO_4+2NaHSO_3$$

(H. Brunck and Graebe, Ber. 1882, vol. xv. p. 1783.)

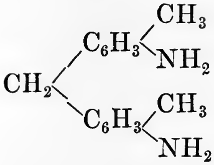
TRIPHENYLMETHANE DYESTUFFS.

P. 110. *Cyanine B* is prepared by oxidation of the sulphonic acids of meta-oxytetralkyldiamidotriphenylcarbinol. (Germ. Pat. 60961.)

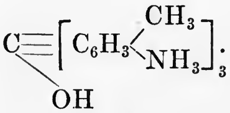
It is a greenish-blue dyestuff, tolerably fast to soap and light, and recommended as a substitute for indigo-extract.

P. 112. *New Magenta.*—This product is prepared commercially by the synthetic process outlined on p. 112.

Anhydroformaldehyde-aniline, $C_6H_5-N=CH_2$, is heated with a mixture of orthotoluidine and its hydrochloride to 100°. Aniline splits off, and diamido-ditolylmethane



is formed. On further heating with ortho-toluidine, hydrochloric acid, and an oxidising agent, a third molecule of ortho-toluidine enters into reaction, the "new magenta" being produced. It is accordingly a salt of triamidotritolyl-carbinol,



New magenta is more easily soluble than ordinary magenta, and dyes a somewhat bluer shade.

P. 128. *Diphenylamine blue.*—This compound has long been considered as triphenylpararosaniline identical with that obtained by phenylation of pararosaniline. Hausdörfer (Ber. xxiii. p. 1961) has compared diphenylamine blue with triphenylpararosaniline, and demonstrated their identity.

P. 130. *New Green.*—Is analagous to Victoria-blue, being the condensation product of dimethylamidobenzophenone with a-phenylnaphthylamine (Germ. Pat. 41756).

The commercial product is a paste. It is principally intended for calico-printing, and gives yellowish-green shades.

P. 138. *Aurotine* is the sodium salt of tetranitrophenolphthaleïn, prepared by nitration of phenolphthaleïn in sulphuric or acetic acid solution (Eng. P. 3441, 1889). It dyes wool either from an acid bath or on a chromium mordant, producing orange-yellow shades fairly fast to light and washing.

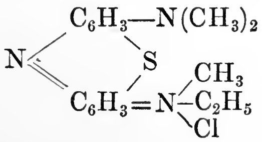
P. 142. *Cyclamine.*—On heating dichlorfluoresceïn with sodium sulphide in aqueous solution, a thiodichlorfluoresceïn is formed. This is converted into a tetraiodthiodichlorfluoresceïn by action of iodine, and the sodium salt appears in commerce as cyclamine. It dyes bluish-red shades resembling those obtained with phloxine. In general the thio-derivatives dye bluer shades than the corresponding fluoresceïns.

P. 143. *Violamine* (*Fast acid violet*), *R & B.*—These dyestuffs are obtained by action of ortho- and para-toluidine respectively on fluorescein-chloride. (Germ. Pats. 49057, 53300, 1889.)

The Violamines are used for wool and silk, and give shades fast to alkalies and light.

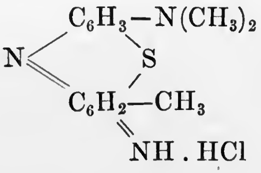
QUINONEIMIDE DYESTUFFS.

P. 158. *Thionine blue G O.*—This dyestuff is closely allied to methylene blue, and its constitution is expressed by the formula:



It is prepared by oxidation of dimethylparaphenylenediamine-thiosulphonic acid (see Methylene Blue) with ethyl-methylaniline, and boiling the resulting insoluble green compound with zinc-chloride solution. A leuco-compound is formed, and is converted into dyestuff by oxidation. The commercial product forms a reddish-brown powder.

Toluidine Blue.—This body is also an analogue of methylene blue, the dimethylparaphenylenediamine-thiosulphonic acid being oxidised with ortho-toluidine. The hydrochloride has the constitution expressed by the formula:

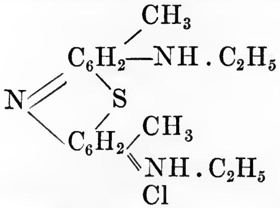


The commercial product is the sulphate and forms a dark green powder, easily soluble in water forming a bluish-violet solution. In dyeing, toluidine blue gives redder shades than methylene blue.

Methylene Blue N.—This dyestuff is a recent member of the series, and is obtained from ethyl-ortho-toluidine in the same manner as methylene blue from dimethyl-aniline.

It dyes redder shades than methylene blue.

Its constitution is expressed by the formula:



Thiocarmine.—This compound is a sulphonic acid of the methylene-blue series, and is obtained from ethylbenzylaniline-monosulphonic acid. Thiocarmine is an acid dyestuff and produces very pure greenish shades of blue on wool, which are, however, not very fast to light.

(English Patents, 4596 and 19065, 1890.)

P. 161.—The oxyindamines and oxyindophenols (Fast Blue, Gallocyanines, &c.) are characterised by the ease with which they react with amines of the fatty and aromatic series, and certain compounds resulting from such reactions have appeared in commerce.

Cyanamines.—This name has been given to the compounds resulting from the action of ammonia and amines in presence of an oxidising agent on Fast Blue R. (A description of Fast Blue R or Naphthol Blue occurs on p. 161.)

Ammonia-cyanamine has a greener shade than the original fast blue; the dimethylamine-cyanamine is more valuable on account of its pure greenish-blue shade.

It has been demonstrated that the green shades of fast blue contain one of these cyanamines; the formation of which results from the interaction of fast blue R with the dimethylparaphenylenediamine formed during the reaction. (Schlarb. Chem. Zeit. 1891, pp. 1281 and 1318; Witt. Ber. 1890, xxiii. p. 2247.)

P. 165. *Delphine Blue and Gallic Indigo* are sulphonic acids of compounds obtained by heating gallocyanine with aniline and analogous bases. The constitution of these bodies has not been determined; they are not simple anilides of gallocyanine, as a carboxyl-group splits off during the reaction.

These dyestuffs are employed in calico-printing, giving pure blue shades when applied with chromium acetate. (Germ. Pat. 55942, Sept. 27, 1889; 50999, July 23, 1889.)

Wool Greys.—These dyestuffs are obtained by action of aniline and analogous bases on the condensation-products of nitroso-dimethyl- and diethyl-aniline on Schaeffer's β-naphtholsulphonic acid.

AZINE DYESTUFFS.

Fast Black.—The commercial product bearing this name is obtained by action of nitroso-dimethylaniline on meta-oxy-diphenylamine. It contains the groups characteristic both of the oxyindamines and the azines. It is a basic dyestuff, and is fixed on cotton prepared with sumac and acetate of iron.

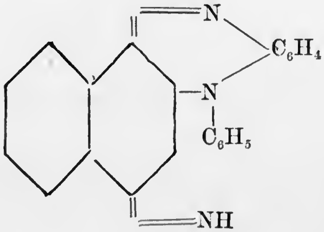
Malta Grey and Nigrisine are bodies of unknown constitution prepared by heating nitrosodimethylaniline hydrochloride in aqueous or alcoholic solution.

Methylene Grey is a similar solution obtained by oxidation of dimethylparaphenylene diamine.

(German Patent, 49446, Feb. 2, 1889.)

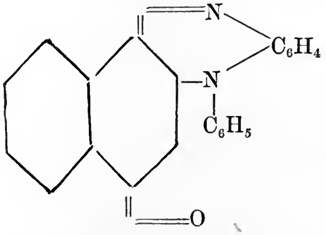
INDULINES AND NIGROSINES.

The simplest Induline of the naphthalene series, rosinduline *par excellence*, is formed by heating benzene-azo-α-naphthylamine with aniline in alcoholic solution under pressure. Rosinduline base forms reddish-brown crystals, M.P. 198°–199°. Its constitution is expressed by the formula:



Accordingly the compound described on p. 205 is a phenyl-rosinduline.

On heating with hydrochloric acid, rosinduline yields ammonia and rosindulone, a compound having the constitutional formula:



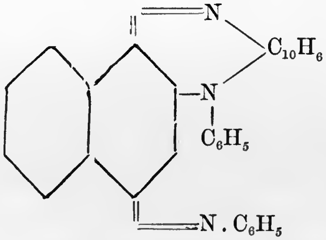
Some of the sulphonic acids of rosindulone are now prepared commercially, and come into commerce as Rosindulines.

Rosinduline 2 B dyes wool bluish red from an acid bath.

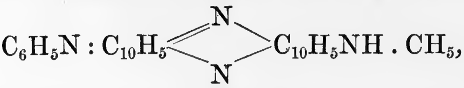
Rosindulines 2 G and G produce orange-red and scarlet shades respectively, and when dyed on silk exhibit a fine yellow fluorescence.

On heating benzene-azo-*a*-dinaphthylamine with aniline, naphthyl and isonaphthylrosindulines are formed.

Isonaphthylrosinduline has the constitution expressed by the formula:



An anilide of isonaphthylrosinduline having the formula



$$C_6H_5N : C_{10}H_5 \begin{array}{c} N \\ \\ N \end{array} C_{10}H_5NH . CH_5,$$

is formed along with phenylrosinduline when benzene-azo-*a*-naphthylamine is heated with aniline.

Naphthyl blue is probably a salt of a sulphonic acid of amidoisonaphthylrosinduline, and naphthyl violet is a dyestuff of similar character. They are principally intended for silk, on which they show a red fluorescence.

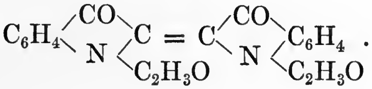
(O. Fischer and E. Hepp, Annal. cclxii. pp. 237–264; H. v. Perger, Mittheil. Techn. Gewerbemuseums, 1891, pp. 202–253.)

INDIGO.

A process in the preparation of indigo from the plant consists in macerating the plants in water and subjecting the liquor to the action of air in presence of ammonia. This "ammonia process" is said to give larger yields and a product of greater purity.

Diacetylindigo.

On heating indigo blue with acetic anhydride, sodium acetate, and zinc powder, a diacetylindigo white is obtained. On oxidation with nitrous acid in presence of acetic acid, diacetylindigo blue is formed. This compound forms small glittering red crystals, soluble in benzene with a beautiful red colour. Its constitution is expressed by the formula:



$$\begin{array}{cccccc} & \diagup CO \diagdown & & & \diagup CO \diagdown & \\ C_6H_4 & & C = C & & & C_6H_4\;. \\ & \diagdown N \diagup & & \diagdown N \diagup & & \\ & & \diagdown C_2H_3O & & \diagdown C_2H_3O & \end{array}$$

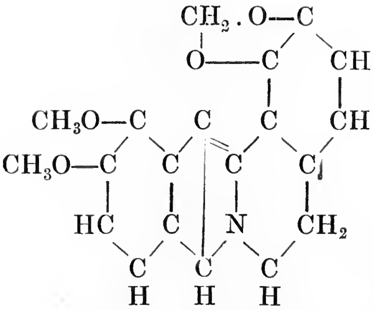
Indigodisulphonic Acid.

The mechanism of the reactions involved in the synthetic process for preparing this compound has been explained by Heymann (Berl. Ber. 1891, p. 3066). The yellow solution resulting from the action of the sulphuric anhydride on phenyl-glycine contains the sulphonic acid of indoxyl-sulphuric ester. On dilution of this solution, oxidation is effected by the sulphuric anhydride.

QUINOLINE AND ACRIDINE DYESTUFFS.

Berberine.

Extensive researches on the constitution of berberine have been made by W. H. Perkin, Jun. (Chem. Soc. Journal, 1890, p. 991). Berberine is allied to papaverine, hydrastine, and narcotine; it is a derivative of isoquinoline, and has probably the constitution expressed by the formula:—



On oxidation with potassium permanganate, berberine yields the following series of compounds, all containing the twenty carbon atoms of berberine intact:—

Oxyberberine, M.P. 198–200°	$C_{20}H_{17}NO_4$.
Dioxyberberine	$C_{20}H_{17}NO_6$.
Berberal, M.P. 149°	$C_{20}H_{17}NO_7$.
Anhydroberberic acid, M.P. 237°	$C_{20}H_{17}NO_8$.
Berberic acid, M.P. 177–182°	$C_{20}H_{17}NO_9$.

DYESTUFFS OF UNKNOWN CONSTITUTION.

Patent Fustine.

Some compounds bearing this name have appeared in commerce. They are prepared by action of diazo-compounds on a decoction of fustic. They are applied in the same manner as fustic.

Fisetin, Quercitin, and Rhamnetin.

Herzig (Monatshefte f. Chem. 1891, pp. 172, 177) has demonstrated that a close relationship exists between these compounds, and the formulæ given on pages 254–256 have to be modified. The molecular weight of quercitin was determined, and from this and analytical data the formula for quercitin appears to be $C_{15}H_{10}O_7$. Rhamnetin is a monomethylquercitin. Quercitin is a hydroxyfisetin, and the formula proposed by Schmid for fisetin has to be altered according. Analyses of fisetin, its acetyl, methyl, and ethyl derivatives prove that the correct formula is $C_{15}H_{10}O_5$. On oxidation by air in alkaline solution, fisetin yields resorcin and protocatechuic acid, while quercitin under similar conditions yields phloroglucin and protocatechuic acid, these results being in accordance with the idea that quercitin is a hydroxyfisetin.

Orceïn.

(Zulkowski & Peters, Monats. f. Chem. 1890, p. 227.)

A study of the process by which orceïn is formed from lichens, by action of ammonia and air, shows that three colouring-matters are formed, viz., orceïn, a yellow crystalline compound, and an amorphous body resembling litmus.

Pure crystallised orceïn is insoluble in water, ether, and benzene; soluble in alcohol, acetone, and acetic acid. Pure orceïn possesses nearly two hundred times the tinctorial power of orchil extract.

The composition of orceïn is expressed by the formula $C_{28}H_{24}N_2O_7$, and its formation may be expressed by the equation

$$4\,C_7H_8O_2 + 2NH_3 + 6O = C_{28}H_{24}N_2O_7 + 7H_2O.$$

The yellow compound has the formula $C_{21}H_{19}NO_5$, and is probably formed according to the equation

$$3\,C_7H_8O_2 + NH_3 + 3O = C_{21}H_{19}NO_5 + 4HO.$$

It was found that the formation of orceïn from orcin is much more rapid in presence of hydrogen peroxide; other oxidising agents did not give favourable results.

No compound of the orceïn class can be obtained from resorcin by action of hydrogen peroxide and ammonia. From a mixture of resorcin and orcin a mixed orceïn, "Reso-orceïn," $C_{20}H_{20}N_2O_7$, is formed.

ALPHABETICAL INDEX.

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