An Investigation of the Metallic Derivatives of Ortho-Substituted Azo Compounds.

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ABBREVIATIONS.

B.P.,	British Patent.
Ber.,	Berichte der deütschen Chemischen Gesselschaft.
Bull.Soc.Chim.,	Bulletin de la Societe Chemique de France.
C.I.,	Colour Index.
Chem.Revs.,	Chemical Revues.
Gazz.Chim.Ital.,	Gazzetta chimica italiana.
J.C.S.,	Journal of the Chemical Society.
J.pr.Chem.,	Journal für praktische Chemie.
Jour.Inst.Chem.,	Journal of the Institute of Chemistry.
J.S.D.C.,	Journal of the Society of Dyers & Colourists.
Mell.Text.,	Melliand Textilberichte.
Z.Anorg.Chem.,	Zeitschrift für anorganische Chemie.

INDEX of COMPOUNDS.

o-Aminophenol. 73, 118.
o-Aminophenol-p-sulphonic acid → B-naphthol. 46, 102.
1-Amino-2-naphthol-4-sulphonic acid → 1-naphthol. 51, 106.
Aniline → B-naphthol-o-sulphonic acid. 39, 98.
o-Anisidine → B-naphthol. 59, 109.
Anthranilic acid → B-naphthol 63, 83, 112.
Anthranilic acid → 2-naphthol-3-6-disulphonic acid. 65, 114.
Benzene-azo-B-naphthol. 36, 93.
Chrome Brown T.V. 76, 121
Chrome Fast Cyanine. 51, 53, 106.
Chrome Fast Violet B., 46, 102.
Crystal Scarlet. 81.
Eriochrome Blue Black B. 51, 107.
2-Hydroxy-5-nitrobenzeneazo-B-naphthol. 43, 100.
2-hydroxy-5-nitrobenzeneazo-B-naphthol-6-sulphonic acid. 48, 54, 103.
2-Hydroxy-5-nitrobenzeneazo-1-naphthol-5-sulphonic acid. 49, 105.
Neolan Blue G. 51, 107.
4:2:1-Nitroaminophenol. 73, 118.
p-Nitrobenzeneazo-B-naphthol. 36, 95.
Orange II. 38, 81, 96.
Ponceau 4 G.B. 38, 81, 98.
Solochrome Red B. 65, 114.
Sulphanilic acid B-naphthol. 38, 96.
Toluylene Brown G. 69, 116.

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PREFACE.

The metallic derivatives of dyestuffs have become quite an important class of colouring matters within recent years. The object of the research described in the pages which follow was to study some aspects of the general problem in chemistry presented by these compounds, with respect to their methods of preparation, their chemical properties and constitution. Throughout the work the technical connection was kept in mind and this may have resulted in an appearance of discontinuity in the subject matter of the thesis, from a chemical standpoint. This is due largely to the fact that one has to rely almost entirely on patents for information and these are concerned with giving an account of successful rather than coherent work upon the subject.

METHODS OF MORDANT DYEING.

Bancroft in his famous book on Permanent Colours defines mordant dyestuffs as "those colouring matters which are incapable of being fixed, or made to display their proper colours without the mediation of some earthy or metallic basis", and though he penned his definition two hundred years ago it is as accurate and concise as any other that has appeared since then. It used to be thought that the mordant had a corrosive effect upon the fibre, eating away the surface and so allowing the dyestuff to penetrate but it is now considered to function by first combining with the wool and then with the dyestuff or by forming an insoluble compound with the colour in the interior of the fibre.

When wool is boiled with certain salts, dissociation of the latter results and the metallic hydrate combines with the wool. For the purposes of this work, chromium is the only mordanting metal which needs to be considered in detail. It can be applied in several ways.

CHROME MORDANT PROCESS. In this process the material is mordanted first, then dyed in a separate bath. Bichromate is used as the mordant but usually an "assistant" is also added, for if boiled along with wool only a little dissociation of the salt takes place. The assistants fall into two classes depending on whether they give a reduced or an unreduced mordant. The former consists of organic substances - cream of tartar being the most satisfactory - which reduce bichromate to the chromic state and are used particularly with those colours which would be destroyed by the oxidising action of bichromate. The unreduced mordant is obtained by boiling bichromate with an acid, usually sulphuric acid, when the chromium is absorbed by the wool mostly in the form of chromic acid - though the reducing power of wool is sufficient to convert some of it to one of the hydrated forms of chromium oxide. It follows that such a mordant will be most satisfactory when used with a colour which develops its full shade only after oxidation, for it is the basic oxides of chromium that combine with dyestuffs.

AFTER-CHROME PROCESS. The class of dyes for which this method is most popular are the azo-mordant dyes. This also/

/also is the group of dyestuffs with which this research is concerned.

They are applied to the unmordanted wool in the same way as the ordinary acid dyes and they must be taken up from an acid bath with good exhaustion; for one advantage of this process is that the bichromate can be added to the exhausted dye bath, thus reducing the amount of labour necessary. As a rule, it gives a faster colour than the chrome mordant process since there is less chance of any free dyestuff being left to wash or rub off - provided the dyebath was well exhausted. The range of the method is limited chiefly by the fact that the final shade is usually quite different from that of the original dye and since it does not develop till the mordanting process is complete, it is obviously difficult to match to shade. This disadvantage is least with dark colours and the process therefore finds one of its main uses in the application of the chrome blacks, such as Diamond Black P.V.

The method is also used for o-hydroxyazo dyes. These dyes are usually not suitable for dyeing on wool already mordanted with chromium as the reaction between them and the insoluble chromium salt is too slow at the temperature of the dyebath. They are usually applied as acid dyes and after treated with the chrome mordant in the same bath. The use of trivalent chromium salts for this purpose is seldom of/

/of any use and bichromates are nearly always employed. This complicates the process as oxidation of the dye usually takes place before lake formation. According to Kopp (Bull. Soc. Ind. de Rouen. Mar-April, 1935. 120-132) Acid Chrome Blue Black NB (C.I. 201) when dyed in an acid bath gives a dull claret shade which when after treated with bichrome passes through a series of colour changes to reach a blue-black. If, however, the chroming be carried too far, it turns to a greyish brown and is finally almost destroyed. At no stage is the shade obtained comparable with that got by dyeing with the chrome complex obtained by the action of chromium formate on the dye solution, which is a pure blue. It is usually quite impossible to separate the two phases of oxidation and lake formation. Owing to this double action of bichromates, dyeing with them is always rather uncertain and empirical and the matching of shades is in many cases a matter of great difficulty.

METACHROME PROCESS. In the literature of dyeing, different authors have put forward different chemical explanations of this process. Briefly, the method consists in adding dyestuff and mordant to the bath simultaneously. The mordant used is sodium chromate and an ammonium salt.

One explanation of/

/of the chemistry of the process (Matthews. Application of Dyestuffs) is that, at the comparatively cold temperature at which the dyeing is started there is no dissociation of the ammonium salt and no formation of the colour lake. Gradually however the acidity of the bath is increased, by the ammonia being carried off with the steam, until conditions favourable to the precipitation of the colour lake are reached. By this time the dye has been absorbed within the fibre so that formation of the colour lake takes place there. The explanation of Horsfall and Lawrie (Dyeing of Textile Fibres) is that the dyestuffs applicable by this method can form chrome lakes, in the presence of the ammonium salt, which are simultaneously absorbed by the wool. They also suggest that the development of acidity is not due to the dissociation of the ammonium salt by heat but that a chemical reaction takes place, presumably with the chrome lake, whereby ammonia is set free. Morgan (JSDC.42,56 (1926)) explains it as firstly a case of double decomposition by which ammonium chromate is formed and then dissociates slowly.

$$Na_2CrO_4 + (NH_4)_2SO_4 = Na_2SO_4 + (NH_4)_2CrO_4$$

$$2(NH_4)_2CrO_4 = 4NH_3 + H_2O + H_2Cr_2O_7$$

Thus there is a gradual production of chromic acid which is reduced by the wool to basic chromic hydroxide and this combines on the wool with the acid dye to form the lake "in situ". The number of dyes which can be applied in this way is very limited. Originally the process was restricted to some colours derived from picramic acid but it had such obvious practical advantages that empirical attempts were made to extend its range. There is now a mixed collection of dyestuffs which, due to one circumstance or another, can be applied in this way. This empirical application of the process may account for the divergence in the chemical explanations advanced.

There are various other one bath methods of mordant dyeing of less importance. The Chromosol mordant depends on the fact that concentrated solutions of bichromate and oxalic acid react together giving, probably, the double salt sodium chromi-oxalate and this compound can be used in a similar way to the Metachrome mordant, with some colours. It is distinguished by having no oxidising action. Another method is to treat the wool with bichromate and formic acid in the bath for 1½ hours at 160°F and then to add the dye. The theory, in this instance, is that the formic acid drives the chromium on to the wool before the dye is added and thus/

/thus prevents precipitation of the colour lake in the bath. These one bath processes approach nearest to the latest method of mordanting, to which the research work about to be described is related. Briefly, it consists of the use of a soluble chromium derivative of the dye which can be applied like a substantive colour from an acid bath. A more complete description of the process is given later with an abstract of the patent literature on the subject.

As a mordant metal, copper is not very important. There are two general methods of application :-

(1) After-treatment of the dyed wool in a bath containing copper sulphate.

(2) Dyeing in one bath with a mixture of the colour and copper sulphate.

The use of copper as a mordanting agent has the disadvantage that the reaction with the dyestuff may not be completed in the bath and consequently the shade may change during the hot finishing operations.

SURVEY OF THE PATENT LITERATURE.

A study of the patent literature dealing with the metallic derivatives of azo-mordant dyes brings out many points worthy of investigation, indicates the wide scope of a research upon this subject and emphasises the properties which make these compounds important in dyeing.

There are various processes for the production of metallic complexes of azo dyestuffs but in general they are prepared by heating the parent azo dye, in solution or suspension, in a medium which may be neutral, acid or alkaline according to the particular case, with a metallising agent that reacts with the dyestuff under these conditions. The Badische Anilin and Soda Fabrik Company was the first to take out patents for the production of these compounds. Their method consisted in boiling the chromable azo dye with such salts as the fluoride, chloride, acetate or formate of chromium. They state that when salts of mineral acids are used an acid binding component, such as sodium acetate, should be added. This company however, visualised these complexes as being useful only for cotton printing and the manufacture of pigments and inks, whereas their present importance is due to their use/

/use as acid dyestuffs for wool and to a limited extent for other fibres. This development was due to the Society for Chemical Industry in Basle who took out the first patents for it in 1915. (Neolan Dyes.)

At this early stage the complexes were prepared by obvious methods. The following for example, from B.P.15064/15 is typical :- Chromium fluoride and the commercial dye from 4:2:1 nitro-diazo-phenol and 1:8 - amidonaphthol - 3:6 - disulphonic acid are boiled for one hour during which the solution changes in colour from red to blackish blue. Anhydrous sodium acetate is added and the mixture boiled for quarter of an hour, then filtered hot. Filtrate is evaporated, salt added, and left to crystallise for at least 12 hours. The green chrome compound which separates is filtered, washed with brine and dried. An interesting method is that of B.P.15456/15 in which aqueous solutions or suspensions of o-amino-phenols, or - naphthols, are boiled with chromic oxide, or a salt of it, and the resulting chrome compounds diazotised by the usual methods. Thus the metallic compounds of o-hydroxy diazo bodies are prepared and if they are coupled to components which contain mordant groups the resulting dyestuffs do not contain the maximum/

/maximum proportion of metal. Such metallic derivatives are known as "half-chrome compounds". This subject is dealt with more fully later (see page 72).

The trivalent salts of chromium are preferred as metallising agents but special cases have caused special chroming agents to be patented. A concentrated alkaline solution of chromium hydroxide i.e. a chromite, is often used and more details of this method will be found on page 40. Chromic oxide, or any of the hydrated forms such as $Cr_2 O_2 (OH_2)$, especially when in colloidal form, is suitable in many instances or chromic chromate, $Cr_2 O_3 \cdot CrO_3$, which is prepared by the action of reducing agents - sodium thiosulphate or alcohol are specified - on bichrome. The above reagents form with dyestuffs, products similar to those obtained when trivalent chromium salts are used but they give higher yields in some cases than the chromic salts. There are however some metallising agents that are preferred because of the peculiar products that result. Thus it is claimed that the complexes formed when basic chromic sulphate is used differ, in tinctorial properties, from those prepared with normal chromic/

/chromic sulphate; that when a chromable azo dye is boiled with the chromium salt of an organic acid, such as chromium benzene sulphonate, the metallic derivative obtained gives brighter dyeings than those prepared in any other way; and that a chromable azo dye can be made to combine with the chromium complex of the same or another azo dye, to give compounds which are described as intermediate products of the hitherto known chromium complexes.

An interesting theoretical discussion arises out of the statement in B.P.356716, that the metals suitable for the preparation of metallic complexes are those having atomic weights between 52 and 59, together with aluminium, zinc, copper and vanadium. This could be expressed more neatly by saying they are the elements with atomic numbers between 22 and 30 inclusive and also aluminium; which leads to the question, what is the connection between aluminium and the elements with atomic numbers between 22 and 30? In the fourth period of the periodic table there are ten "transition" elements (At Nos.21-30) the first of which, scandium, atomic number 21, is not a/

/a mordant metal. The element with atomic number 31 is gallium of group III B., which is not a mordant metal either, but the metal directly above it in group III B, and therefore closely related to it, is aluminium. Thus the inclusion of aluminium does not constitute a break in the close relationship that exists among the mordant metals. Their similarity is further shown by the graph of atomic numbers against atomic volumes, for the nine elements from the fourth period occupy one of the minima and the adjacent one is occupied by aluminium. This fact, that these metals have small atomic volumes, and consequently a comparatively strong attraction for planetary electrons, facilitates the forming of co-ordination compounds by them and so is a strong confirmation of the generally accepted theory that mordanting is a process whereby the dyestuff forms a co-ordination compound with the metal (see page 21).

In many of the patents it is recommended to add compounds other than the metallising agent and the dyestuff, in order to obtain special results. In some of these cases the mechanism by which this effect is produced is not at all obvious. B.P.364147 and 384767 claim that/

/that "chromium complexes which are intermediate products of the hitherto known compounds can be prepared by treating dyes from 1-amino-2-naphthol-4-sulphonic acid, or its nitrated derivative, and α- or B-naphthol, with a chroming agent in presence of a proportion of alkali metal ions which has not a salting out effect, until there has been formed a dye which is not precipitated by addition of a saturated solution of common salt." Such products are very soluble in water and give very level dyeings with good exhaustion. They differ from the normal complexes by giving a precipitate in dilute sulphuric acid solution and so cannot be applied to fibres in the usual way. Sodium formate or bisulphite are quoted as suitable sources of alkali metal ions, and the optimum proportion varies with the dyestuff used. It is difficult to see what can be the action of the alkali ions in a case like this. Some work is described later (page 53) on a dyestuff which is a derivative of 1-amino-2-naphthol-4-sulphonic acid though not done with this problem in mind, and it is shown there that more than one chromium compound can be obtained from the same dyestuff. This last point which seems an important one to the writer, is stressed much/

/much more in the patent than in the chemical literature on the subject.

Organic substances such as glucose, starch or glycerine are often added especially when the preparation is in a strongly alkaline condition for they are said to protect the dye from the action of the alkali and to act as protective colloids preventing premature precipitation of the chromium hydroxide. The metallic derivatives of compounds with no solubilising groups are often prepared in the presence of nitrogenous organic liquids, aniline and pyridine being the commonest but many of their analogues and triethanolamine have also been mentioned. The organic derivatives of ammonia seem to be the best organic solvents for metallic complexes.

Other interesting points gathered in a survey of the patent literature include the statement that by treating with a metallising agent a mixture of different dyes containing mordant groups, there is formed a complex which contains the residues of several dyes linked to a central/

/central metal. This is similar to the product obtained by making a mordant colour react with the metallic derivative of another mordant colour.

Before closing this survey, the distinction between "primary and secondary chromium complexes" defined in B.P.446,820, should be mentioned. The first patent dealing with metalliferous azo compounds (see page 8) specified that when the salts of mineral acids are used as metallising agents, acid binding components such as sodium acetate must also be added. This remained an undisputed statement, at least with respect to chromium complexes, till 1931, when another patent claimed that mineral acid not only favoured the reaction but that sometimes the reaction could be hastened by addition of mineral acid. The compounds so prepared, called secondary chrome complexes, differed from those previously obtained. The process was further explained in B.P. 446820 where it was said that the formation of these new chrome compounds takes place in two phases :-

(1) Primary chrome complexes are formed by reactions in a neutral or very slightly acid medium and are identical with the products of processes in which neutralisation of the/

/the liberated acid is effected.

(2) Under prolonged action of the chroming medium rendered strongly acid by the mineral acid derived from the chromium salt, and if desired by the previous addition of acid, the primary compounds are converted into secondary chrome complexes. The latter are characterised chiefly by their greater resistance to acids of all kinds and by giving brighter, more even and faster to light shades when dyed. The scope of the reaction is wide since all ortho-hydroxy-azo dyes which can be converted into primary chrome compounds can be transformed into secondary ones by treating the former with mineral, organic or sulpho-aromatic acids in the absence of substantial amounts of chroming agents. The transformation takes place particularly well in the absence of neutral electrolytes - which shortens the time and permits a lower temperature of reaction.

The results of some experiments dealing with this subject are described later (page 54).

Patents Quoted Above.

Copper Derivatives :- B.P. 1611/15; 12249/15; 13204/15; 15127/15. 16916/15

Metallising Agents :- B.P. 104045; 116535; 260830; 303384; 384767; 369991;369936; 355800; 356716.

Additions :- 272918; 271897; 295594; 297687; 35169; 356716; 364147; 384767.

Primary & Secondary Complexes :- 446820; 365113; 358146.

Miscellaneous :- 297331; 15064/15; 15456/15.

Behaviour of Metallic Complexes in Dyeing.

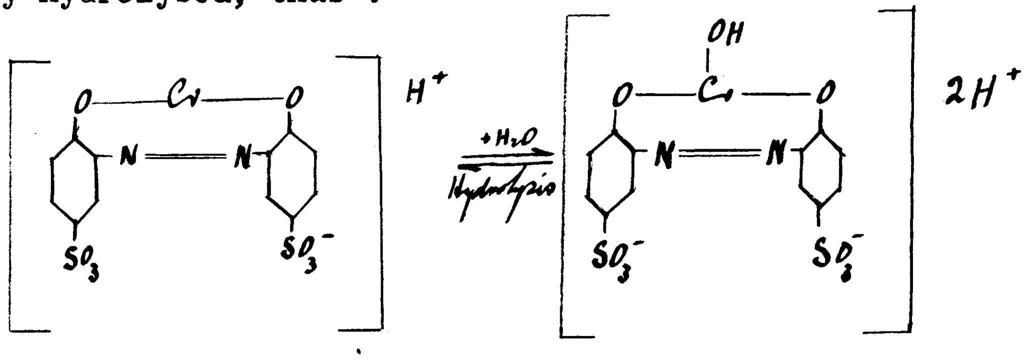
In the use of these metallic derivatives as dyestuffs there are two stages. The material is boiled with the colour and 4% of sulphuric acid for half an hour, during which time the dyestuff penetrates within the fibre. But in order to develop fully the shade and fastness properties of these colours it is necessary to add another 4% of acid and to boil for one and a half hours. No adequate explanation of the change which takes place on the fibre during this period of "development" has yet been evolved, though it is assumed that the soluble metallic dyestuffs are transformed/

/transformed into the insoluble colour lakes presumably through a reaction with the wool substance.

Since this is a very important property of these compounds it is as well to consider some of the explanations that have been suggested; but before doing so it should be mentioned that there is an alternative method of development. This consists in replacing the second 4% of acid by 1.5% of sodium benzene sulphonate which is said to catalyse the development of these colours.

There are three general ways in which these dyestuffs might combine with wool. The sulphonic acid groups of the dye could react with the basic groups in the wool, the mordant metal not being implicated in any way; or there might be ionic combination between the mordant metal and the carboxylic groups in the wool. The third possibility is that the wool substance combines with the mordant metal by co-ordination. With such a complicated substance as wool it is not unlikely that all three methods are used to some extent. The similarity which these colours bear to ordinary acid dyes - in so far as their absorption by wool is concerned - points to the first method being used but their fastness properties indicate in a qualitative way/

/way that the metal is involved in the combination with the fibre. The subject has been investigated by Ender and Muller (Mell Text.1938. See J.S.D.C.1938;54;190,243 and 289) with reference to chromium compounds. They start by claiming that the free acids of these compounds are amphoteric, like wool, the chromium being present as a basic monovalent group. The complexes are represented as being similar to the acid salt of a strong acid with a weak base and the complex ion is easily hydrolysed, thus :-



Their experiments then led them to the conclusion that salt formation takes place between the sulphonic acid groups and the basic groups in the wool and also that about 10% of the basic groups in the wool are involved in a complex combination with the chromium in the dye acid. The "developing" action of mineral acid is attributed to a decrease in affinity between the wool and the dyestuff, which retards the/

/the combination between the chrome complex of the dye and the basic groups in the wool by increasing the ionisation of the latter. The sodium benzene sulphonate is said to act in a similar capacity by attaching itself to the dye molecule so that there is less tendency for the wool-dye complex formation.

The above explanation implies that the change by the dyestuff from a soluble to an insoluble body is brought about by the wool substance replacing other molecules in the co-ordination sphere of the metal. In the light of the present knowledge this seems the most satisfactory explanation.

Modern Chemical Theory of Mordant Dyeing.

Werner, in 1908, applied his theory of internal complexes to the problems of mordant dyestuffs and showed that the peculiar arrangements of groups on which mordanting properties depend are analogous to those which confer the ability to form co-ordination compounds. He also found that cloth treated with metallic mordants changed colour when added to solutions of B-diketones and he had already shown that the latter when reacting with metallic salts gave rise to an important class of co-ordination compounds.

The development of the electronic theory was responsible for confirming Werner's suggestions and for giving a more detailed explanation of the mechanism of co-ordination. For the purposes of this research it is sufficient to consider that group of co-ordination compounds which are called "chelate". This term is used to describe those cyclic structures which arise from the combination of metals with organic (or inorganic) molecules that occupy two positions on the co-ordination sphere. The formation of these rings/

/rings may involve either primary or secondary valencies and so they may be divided into three classes, namely, rings formed by two primary valencies, by one primary and one secondary valency, or by two secondary valencies. The names "tridentate" and "quadridentate" are applied to compounds in which the metal atom is linked to the organic molecule through three and four groups respectively and of course each can be subdivided according to the type of valency which is being used. It is not intended to imply that the nature of a bond, in the co-ordination complex, which arises through a primary valency differs in a material way from one due to a secondary valency, even though the former is represented by a full line and the latter by a dotted line or an arrow. The distinction is merely to make clear the number of hydrogen atoms that have been replaced.

Chelate compounds may be either ionised or non-ionised. The colour lakes are placed in the non-ionised section, the members of which are also known as inner complex compounds. The term "secondary valency" has been replaced by the electronic one, "co-ordinate link" and/

/and explained by Sidgwick (Electronic Theory of Valency) as follows :- For a co-ordinate link to be formed atoms of different characters are required. The donor must have a "lone pair" of electrons and must be part of a stable molecule while the acceptor must have room for more electrons. Morgan and his co-workers have studied the application of the co-ordination theory to mordant dyes and found that dyes which can be mordanted with the salts of polyvalent metals have usually a replaceable hydrogen atom and a donor atom so disposed as to be able to form a ring of either six or five atoms connected to the aromatic ring in the ortho position. They have prepared and analysed colour lakes of the following classes of dyes :- o-Amino-o-hydroxy-azo; di-o-hydroxy-azo and mono-o-hydroxy-azo dyes and shown them to be inner complex compounds. Their results will be considered more fully when the dyestuffs of the above groups are dealt with later.

It should be noted however that the work so far described purports to deal with the insoluble colour lakes, the soluble metallic derivatives having been neglected.

According to the theory just described it is difficult to see how there could be any fundamental divergence in the structures of these two types of metallic derivatives and the author is of the opinion that what has been said above applies equally to the soluble derivatives; that, in fact, the compounds which have been called colour lakes, by Werner, Morgan and others, among the azo-mordant dyes are analogous to those which have been described in the patent literature as soluble metallic derivatives of dyestuffs. The true colour lakes are probably formed by interaction between these compounds and the wool substance, in some such manner as that already described on page 19.

The substituents which when present in the ortho position to the azo group give rise to mordant properties are mainly the hydroxyl, carboxyl and amino groups, though it is claimed that secondary amino and alkyl -or aryloxy groups can take their place, and it will be seen that each of these groups could result in a univalent chelate molecule, one of the azo nitrogen atoms acting as donor. (There are often other alternatives to/

/to the azo-nitrogen as donor, but this point will be considered later).

Two of the main properties of chelate compounds, which have not yet been mentioned, are the failure of the usual analytical tests for the metals when they are applied to such compounds and the fact that groups involved in chelation are non-reactive.

Survey of Chemical Literature.

It seems advisable, before considering in detail the results of this particular research and their relation to current theories and previous investigations in the same field, to describe some of the work dealing with this subject which has already been published. Sir Gilbert Morgan, in the course of his work on co-ordination compounds, dealt with the metallic derivatives of mordant dyes and his results and conclusions have become authoritative. Therefore the literature can be best summed up, probably, by setting forth Morgan's opinions, then those of other workers who may either agree or disagree with him, and, finally, work done along lines other than those followed by him.

Morgan divides the di-o-hydroxyazo dyes into two classes. Those with which the mordant forms a colour lake of the original dye, he calls "true mordant dyes". The other class is those in which lake-formation is accompanied or even preceded by oxidation. As a true mordant dye Eriochrome Red B(C.I.652) is quoted. It is said to give a/

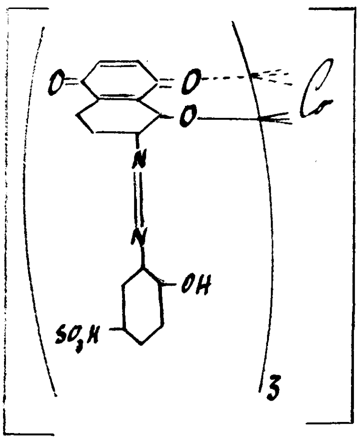
/a chromium compound in which the metal is combined in complex formation with only one hydroxyl group i.e. the metal has replaced hydrogen from this group and become co-ordinated to that nitrogen atom of the azo link which is furthest from the hydroxyl group taking part in the reaction.

Diamond Black P.V. (C.I.170) however, is said to undergo oxidation when mordanted under practical dyeing conditions. Though it gives with chromium fluoride a lake analogous to that of Eriochrome Red B, with a cobaltammine reagent oxidation takes place, the product having formula 1, and this corresponds to the black lake obtained on wool from the dye and a chromic acid mordant.

The o-amino-o-hydroxyazo dye Metachrome Brown B (C.l.101) furnished only the simple cobaltic lake (II), though with excess of cobaltammine an unstable di-cobaltic salt was obtained indicating that the dye may undergo tautomeric change so that the amino group becomes an imino group with a feebly acidic hydrogen.

Since according to the above, one hydroxyl group in the di-o-hydroxyazo dyes is not implicated in the/

/the chelate group, mono-o-hydroxyazo dyes should also be capable of yielding lakes, but here the property of lake formation was in many cases too feeble to be detected. Morgan therefore suggests an alternative general formula (III) for lakes of di-o-hydroxyazo compounds in which the second hydroxyl group is implicated by migration of its hydrogen to one of the azo nitrogen atoms, thus forming a feebly acidic (NH^-) radicle.



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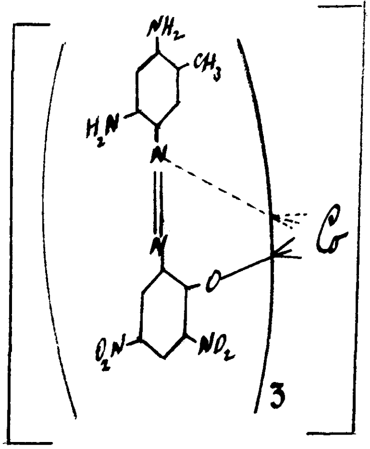

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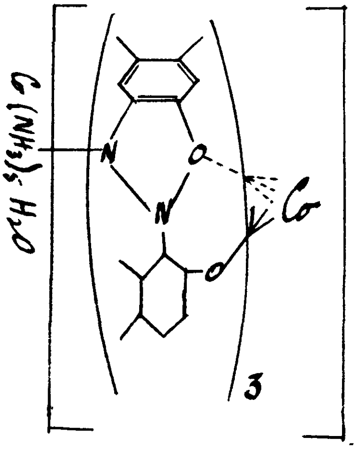


III

The above is a summary of the work and conclusions described by Morgan and Main Smith J.C.S.125,1731 (1924) and J.S.D.C. 41,237 (1925). Five important points can be drawn from it and considered in more detail, comparing each with the results of other investigators in the same/

/same field. These points are :-

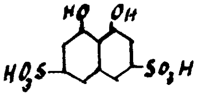
1. Lake formation is less likely with mono-o-hydroxyazo than with di-o-hydroxyazo dyes.
2. Only one hydroxyl group in di-o-hydroxyazo dyes is implicated in the complex formation.
3. Preliminary, or simultaneous, oxidation of dyes in mordanting, with special reference to Diamond Black P.V.
4. Co-ordination of mordant metal to the azo link.
5. Effect of amino group o-to the azo link.

I. It may well be that lake-formation does not take place so readily with mono-o-hydroxyazo as with di-o-hydroxyazo compounds, but other workers do not appear to have found the difference so marked as Morgan and Main Smith. The copper complexes of benzene-azo-resorcinol and of Orange II (sulphanilic acid⟶B-naphthol) and the cobalt derivative of benzene-azo-B-naphthol are described by Pfeiffer etc. (J.Pr.Chem.149, Oct.1937) as typical of this class and there is no implication that they are more difficult to form than the di-o-hydroxyazo derivatives. The same may be said of the results of Drew and Landquist (J.C.S. March 1938, page 292) who prepared the copper complexes of five mono-o-hydroxyazo/

/o-hydroxyazo compounds. According to the present literature on the subject, it may be inferred therefore, that there is no remarkable difference between mono-o- and di-o-hydroxyazo compounds, in general, where the ability to form metallic complexes is concerned.

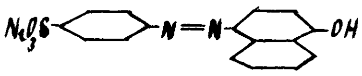
II. It has been held that in the di-o-hydroxyazo complexes only one hydroxyl is implicated (see also Mason, J.S.D.C. 1932, 48, 293) but Drew and Landquist found their work did not confirm this view. On the contrary, they found that 2:2′ - dihydroxyazobenzene and o-hydroxybenzeneazo-B-naphthol gave copper derivatives containing one atom of copper to one azo-group. These results confirm those of Pfeiffer and co-workers. Ender and Muller (their work has already been described in another connection, page 19) found that in chromium complexes each of the o-hydroxyl groups react similarly. Fierz - David and Matter (J.S.D.C. 53 (1937), 432) as a result of both examination and synthesis, propose a structural formula for Chlorantine Fast Rubine R LL which represents it as the copper complex of a di-o-hydroxyazo dye, the metal having reacted in exactly the/

/the same way with each of the hydroxyl groups. The concensus of opinion seems, therefore, to hold that in di-o-hydroxyazo compounds both hydroxyl groups react similarly, in lake formation.

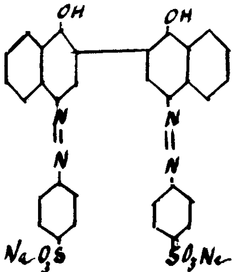
III. Morgan and Main Smith hold that in many cases, particularly Diamond Black P.V. and the Chromotropes (derivatives of chromotropic acid 

), the process of lake formation is accompanied or even preceded by oxidation. Mayer, (Chemie der Organischen Farbstoffe, page 50 (1932)) however, gives two alternative formulae for the chrome lake of Chromotrope 2R. and in neither of them has oxidation been assumed. In the Bull. Soc. Ind. Mulhouse, (1929)95,217, it is disputed that the colour lakes of the Chromotropes are formed by preliminary oxidation of the dye which then combines with the chromic oxide. It is suggested that the dye remains unoxidised but combines with chromic oxide formed by oxidation of the wool. This suggestion, though not very convincing, is supported by the claim that red solutions of Chromotropes become blue when chromic fluoride is added and chromium is not precipitated from the resulting solution by sodium carbonate. Another/

/Another aspect of this question is raised by Lloyd (Jour.Inst. Chem.1937 page 56). He points out that the outstanding property of the chrome lake of Diamond Black P.V. is its remarkable fastness to potting i.e. prolonged treatment with boiling water. This property is not possessed by the chrome lakes of the Chromotropes. Yet the formula suggested by Morgan and Main Smith for the chrome lake of Diamond Black P.V. (cf. formula 1 page 28) resembles very strongly the chrome lake of an oxidised chromotropic acid derivative. But since the properties of these dyestuffs are so different, at least in respect to fastness to potting, it is unlikely that their structures are so similar. Kopp (Bull. Soc. Ind. de Rouen 1935.120-130) draws attention to an unexpected result of oxidation. He says that Orange I (C.I.150) which has the formula (1), is put on the market by the Berlin Aniline Company under the name of Chrome Brown for after-chroming. In this case the intermediate oxidation product is stated to have been prepared in the pure state and to have formula (II) which provides the necessary ~~ortho~~ hydroxy groups.



I

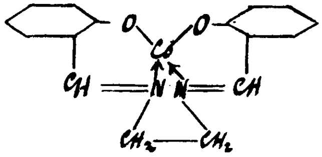


II

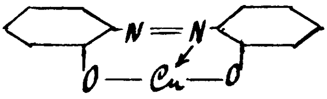
These considerations seem to indicate that the question of oxidation during mordanting is still open.

IV. Tsumaki (Bull.Chem.Soc.Jap.13(1938)2,258) from a study of absorption spectra concludes that in the inner complexes of metals with oxyaldimines (which are analogous to o-hydroxyazo compounds) the metal is attached by a co-ordinate link to the/

/the nitrogen atom, a typical formula being

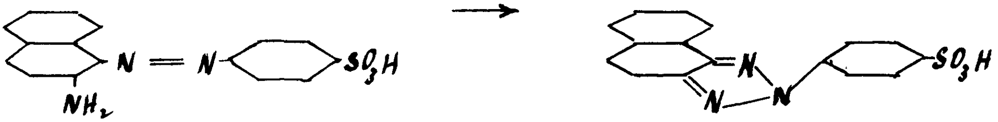


Also from a study of absorption spectra, Blumberger (Chem. Weekblad.,1928,282,315,1930,190;1932,454;1933,538;1935,6) attributes the anomalous behaviour towards mordants of o- and p-hydroxyazo dyes to co-ordination of the metal with the neighbouring azo group. Elkins and Hunter (J.C.S. (1935) 1598) support this and also state that the stereochemical arrangement of the aryl groups about the azo nitrogen atoms is trans. It has also been suggested that the metal is co-ordinated to both nitrogen atoms (see Kopp.Bull Soc.Ind.Rouen, (1935)63,120) but Drew and Landquist have gone into this matter more fully and maintain this to be impossible on stereochemical grounds. They give good reasons for deciding that the metal is co-ordinated to the nitrogen atom remote from the hydroxyl group, a typical formula being.



V. Concerning the effect of an amino group o- to the azo link/

/link, Morgan and Main Smith found that the o-amino-o-hydroxyazo dye Metachrome Brown B gave a metallic complex, but the amino group was not implicated. Pfeiffer and his co-workers state that an amino group o- to the azo link confers lake forming properties just as does an hydroxyl group. In some cases however, oxidation takes place, when the metallic salt is added, with the production of a triazol compound, e.g. sulphanilic acid ⟶ B-naphthylamine when boiled with a copper salt and ammonium hydroxide give a phenylnaphthotriazol :-

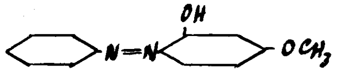


This reaction had been observed earlier by the Italian workers on the subject. Charrier and Beretta (Gazz.Chem. Ital. 56,865(1926)) suggest that the formation of metallic complexes by o-amino-azo compounds is an intermediate stage in the production of triazoles. Even less research has been conducted with the metallic complexes of o-aminoazo compounds than with the corresponding hydroxy/

/hydroxy derivatives, so the question must be left open.

OTHER WORK.

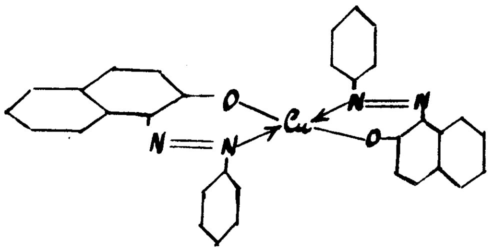
o-Carboxyazo Compounds. Drew and Landquist describe the copper complexes of some o-carboxy and o-carboxy-o-hydroxy-azo compounds and conclude that "an o-carboxyl group resembles an o-hydroxyl, but occasions formation of a less stable link between azo compounds and metal".

Effect of m - or p-hydroxyl groups. Pfeiffer and others, "are convinced that m - and p-hydroxyazo compounds do not give metallic complexes". They prepared the copper derivative of benzene-azo-resorcinol, methylated it, then treated with acid to form the copper free azo dye and examination showed the resulting product to have the formula  which indicates that the p-hydroxyl group was unaffected by the complex formation. Crippa (Gazz.Chem.Ital.(1928)58.716) found that p-hydroxybenzeneazo -B-naphthol gives metallic lakes in which only the o-hydroxyl is involved and Drew and Landquist state that m-hydroxybenzeneazo-B-naphthol behaves in a similar way. Co-ordination of a metal to azo nitrogen, therefore, takes place only when the metal is covalently linked to certain substituents which must be in the o-position to the azo group.

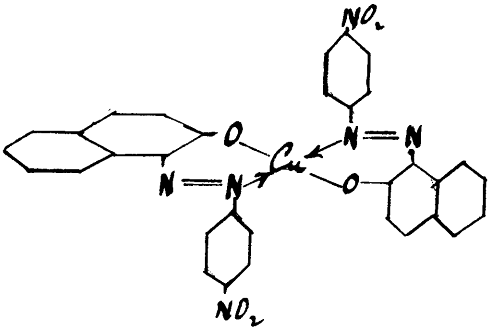
DESCRIPTION OF PRESENT WORK.

Mono-o-Hydroxyazo Compounds.

An outline of the work done on this subject has already been given (page 29) and it has been shown that, according to the literature, mono-o-hydroxyazo bodies form metallic complexes with comparative ease. The copper lakes of benzene-azo-B-naphthol and p-nitrobenzene-azo-B-naphthol (Para Red) were found to contain one atom of copper to two azo groups and so they may be expressed by formulae I and II.



I



II

Since these experiments were made, Drew and Landquist (J.C.S. March 1938, page 292) have described the preparation of the copper lake of benzene-azo-B-naphthol and agree with the above formula. Since these lakes are co-ordinately saturated they/

/they must contain linkages between the copper and the azo nitrogen atoms but taking into account the strain set up, the above writers say that a copper atom cannot be co-ordinated with both nitrogen atoms of an azo group. The salicylideneimines - which have the group $-CH = N-$ in place of the azo group - give similar metallic complexes and in them there can be no dubiety as to which nitrogen atom is responsible for the co-ordinate link. Therefore it is argued by analogy that in the azo complexes the metal is linked to the nitrogen remote from the hydroxyl group. They also conclude that the azo nitrogen atoms are of the anti form and this is supported by other workers already quoted (page 33).

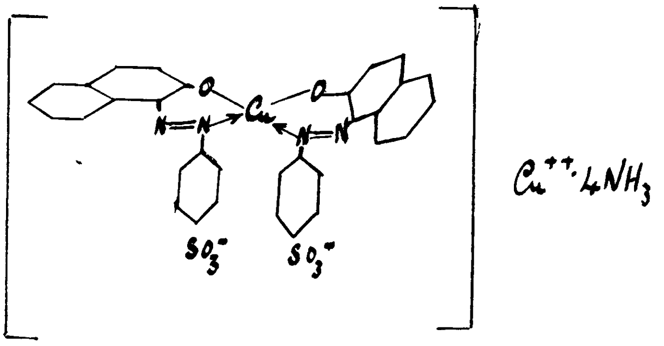
The quinone-hydrazone type of formula may be applied to these azo compounds without causing any alteration in the form of the formulae for the lakes, only the nature of the linkings being changed.

The lakes which are of interest as dyestuffs are, of course, almost exclusively sulphonic acids and so the preparation of the two complexes described above was rather in the nature of an introduction. In each section of the/

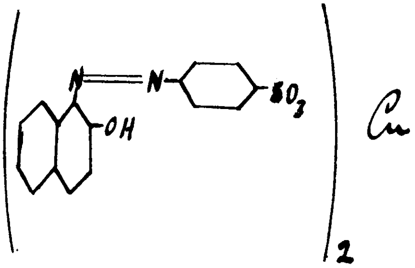
/the research this policy was pursued, viz. the preparation first of lakes of compounds which had no lake forming groups except in the o-position to the azo link and then proceeding to investigate the sulphonic acid derivatives in the light of the knowledge so gained. "Because of the great variety of forms shown by the azo-sulphonic acids and the numerous structural possibilities among their metallic derivatives, the study of these substances presents a complicated problem" (Drew and Landquist). Probably for this reason, almost all the published work which is based on analytical results deals with the lakes of unsulphonated azo compounds. A similar reason no doubt accounts for the paucity of published work dealing with the chromium lakes in a quantitative rather than a qualitative way; for chromium offers more difficulties certainly than copper and probably more than cobalt or nickel.

The copper lakes of sulphanilic acid→B-naphthol (Orange II) and aniline→B-naphthol - 6 - sulphonic acid (Ponceau 4 G.B) were each found to contain one atom of copper to a molecule of the complex. These lakes can be/

/be prepared either by boiling the azo compound with copper sulphate and sodium acetate, or cuprammonium sulphate. The function of the sodium acetate in the first method is to act as an acid binding agent so that no free sulphuric acid is present, for these complexes are decomposed by boiling with dilute mineral acid. It seems that copper cannot enter into complex formation unless the sulphonic acid group is neutralised. This is the only respect in which mono-hydroxyazo compounds have been found inferior in lake forming properties to di-o-hydroxyazo compounds, for some of the latter are quite stable to dilute mineral acid and their free sulphonic acids have been isolated and analysed. When cuprammonium sulphate is used the lake has two molecules of ammonia per molecule of dyestuff and so can be expressed by formula III. The lake from copper sulphate and sodium acetate has a similar structure but is hydrated instead of having co-ordinated ammonia.



III



IV

If copper sulphate alone is added to a solution of Orange II there is produced quite a different product, namely the copper sulphonate (IV). The fact that III contains copper in a chelate ring is shown by adding potassium hydroxide to it, for then only half the copper is displaced and there is formed the potassium sulphonate of the copper complex. This stability of one atom of copper per two molecules to alkali is in accordance with the complex derivatives of simple azo bodies already described.

An attempt was made to prepare the chromium lake of Orange II by the chromite method (page 97). A paste of dyestuff, chromium hydroxide and 30% sodium hydroxide was heated, but from the resulting product only a very small yield of the chromium complex was obtained the rest being unchanged Orange II. This was soluble in water and some of its chromium content was precipitated by ammonium hydroxide, the remainder being stable to alkali and detectable by analytical tests only after the azo group had been reduced by "hydrosulphite". This indicates that it has a structure analogous to the copper complex III/

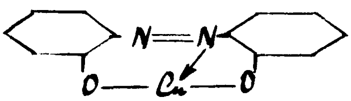
/complex III but the method of preparation is a very unsatisfactory one in this case and did not give sufficient for an analysis to confirm deductions as to structure.

With Ponceau 4 G B, instead of using a mixture of copper sulphate and sodium acetate, copper acetate was used as the metallising agent. The lake has a structure of the same type as III and showed the same reactions except with potassium ferrocyanide. With this reagent no precipitate was obtained until the mixture had stood for some considerable time. Drew and Landquist observed a similar behaviour with some simple azo sulphonic acids and attributed it to the cupric ions being feebly co-ordinated with azo nitrogen atoms. Since in this case however one nitrogen atom in each azo group is already co-ordinated to metal, if the cupric ions are co-ordinated it must be to the nitrogen atoms adjacent to the hydroxyl group. Ponceau 4 G B was the only compound in which this inhibition was observed so there is not sufficient data to attempt a generalisation, though possibly the explanation is connected with the position of the sulphonic acid group relative to the azo group.

o:o'-Dihydroxyazo Compounds.

It has already (page 35) been pointed out that many investigators have shown that the capacity to form inner complexes with metallic salts in which both hydroxyl groups are implicated, distinguishes o:o'-dihydroxyazo compounds from those similar azo bodies in which one of the hydroxyl groups is in the m - or p - position to the azo link.

Drew and Landquist prepared the copper lake of 2:2'-dihydroxyazobenzene and gave it formula I in preference to II because



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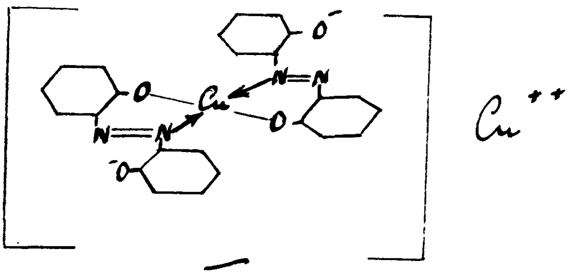


II

(a) The ionised copper atom would be replaceable e.g. by sodium, but this is not so.

(b) Compounds such as II could be formed by substances having the second hydroxyl group in the m -or p-position to the azo link.

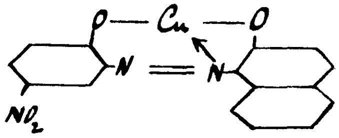
(c) It would be possible for the ionised copper atom to/

/to accommodate four co-ordinating radicles i.e. the compound would be co-ordinately unsaturated to the extent of two co-ordinating molecules or radicles per atom of copper whereas it is only so to the extent of one. Pfeiffer (ibid) had previously decribed the compound and attributed the same structure (I) as above to it and shown by molecular weight determinations that one molecule of the azo compound gives rise to a molecule of the complex. He also proved it to be co-ordinatively unsaturated by combining one molecule of ammonia to the copper which indicates that only one of the azo nitrogen atoms is co-ordinated to the metal. This structure is seen from models to be very little strained, the azo group necessarily of the anti form and the metal associated in a 5 and in a 6-membered ring.

Since these arguments appear fairly conclusive, this method of representing the copper lakes of o:o' - dihydroxyazo compounds has been adopted here.

The first of these azo compounds to be investigated in the present research was 2-hydroxy-5-nitro-benzeneazo-B-naphthol. This compound differs from Para Red - the copper lake of which has been described (page 36) - in having two/

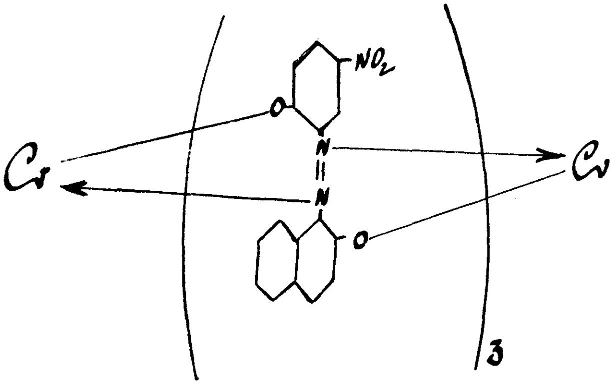
/two o-hydroxyl groups instead of one. A red-brown copper complex was obtained with one atom of copper per molecule formula III.



III

The chromium derivative was prepared by refluxing the azo compound with chromium acetate in alcoholic solution and was found to contain two thirds of an atom of chromium per molecule (formula IV)

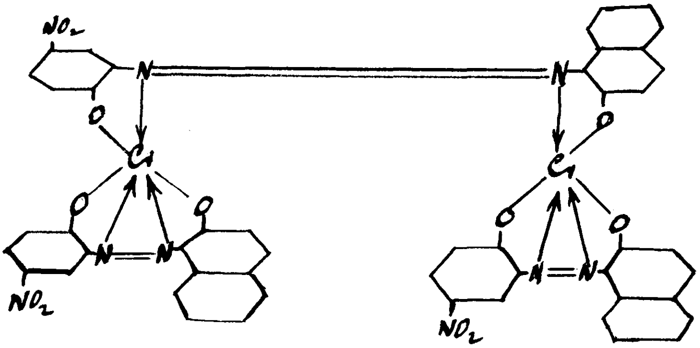
Since the literature on the chromium derivatives is very meagre and this research has not been concerned with elucidating stereochemical details in the structure of these compounds the formulae attributed to them will be of a tentative type in so far as they deal with the degree and nature of the co-ordination bonds. Qualitative tests - particularly on o:o' -dihydroxyazo sulphonic acid lakes, which are soluble in water (see below) - show that all the chromium attached to hydroxyl groups is part of a chelate ring. The simplest way to formulate the above chromium derivative is therefore as follows (IV.A) :-



IV A

This represents each of the metal atoms as co-ordinatively saturated.

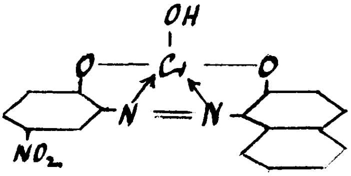
An alternative is represented by IV.B.



IV B.

It will be shown later that in some chromium complexes the metal is present in a monobasic state and it is possible that in this case there is first formed a compound having formula IV.C. Two such molecules might then react with a third molecule of dyestuff to give a derivative of structure IV.B. In support of this it may be mentioned that the patent/

/patent literature several times e.g.B.P.297331



IV C

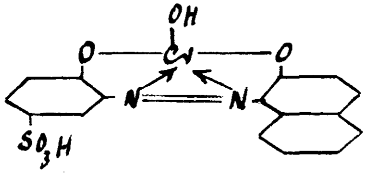
mentions the preparation of complexes by combination of a chromable dye with an already prepared chrome complex.

For simplicity formulae of the type IV.A will be used in the remainder of this report though it is not meant to exclude the possibility of IV.B being a more accurate representation.

The next azo compound to be investigated was that from p-sulphonic acid-o-aminophenol⟶B-naphthol (Chrome Fast Violet B. Colour Index 169). It differs from the previous compound by having a sulphonic acid group in place of the nitro group. The copper complex is obtained as a very sparingly soluble brown powder when copper sulphate is added to a boiling aqueous solution of the dyestuff. Analyses of this compound failed to suggest a satisfactory formula for it. Though the preparation was done three times, on each occasion the product was found to contain 1.3 atoms of copper combined with one molecule of the dyestuff. The difference in properties between this lake - which is only/

/only sparingly soluble in water, alcohol, benzene or other solvents - and the chrome one is striking. The chromium complex is obtained by the action of chromium acetate on an aqueous solution of the dyestuff. Since it is very soluble in water it is obtained by evaporating down and salting out. It is partly purified from salt by extraction with alcohol then evaporating the solution to dryness, for it will not crystallise.

No ionised chromium can be detected in an aqueous solution of the complex by the ordinary reagents which points to all the chromium being in combination with the hydroxyl groups. Analyses indicate that one atom of chromium has combined with one molecule of the dyestuff and the compound is therefore represented as : -

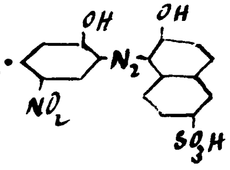


V

It may be that there is normally formed an internal salt between the monobasic chromium group of V. and the sulphonic acid, which is hydrolysed by alkali. This is the suggestion of Ender and Muller (see page 19) but the extreme solubility of the above chrome complex does not entirely support this/

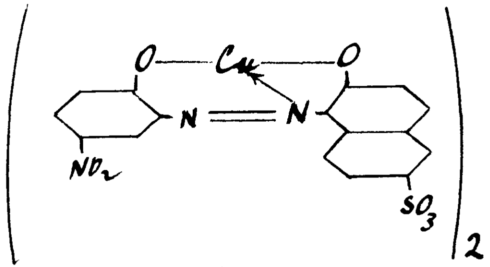
/this, for the chromium compounds of sulphonic acids are not usually very soluble.

2-Hydroxy-5-nitrobenzeneazo-B-naphthol-6-sulphonic acid.

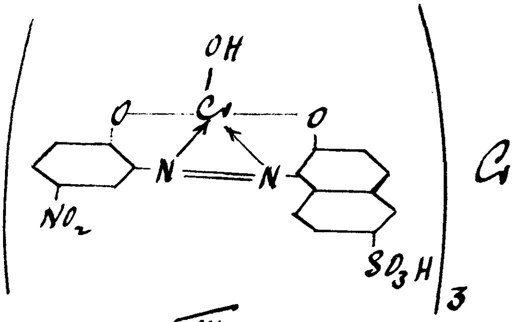


This compound is closely related to the azo body described on page 44, but it has a sulphonic acid group on the naphthalene nucleus. The copper derivative is a brown powder precipitated when copper acetate is added to an aqueous solution of the dyestuff. It is soluble in hot water and has 1.5 atoms of copper to a molecule of dye. Formula VI.

The chromium compound was prepared by refluxing the dyestuff with chromium formate; the dyestuff which was in the form of its sodium salt having been converted into the free acid by the addition of formic acid. The chromium derivative is soluble in water and alcohol, gives a small precipitate of chromium hydroxide with alkali but if the filtrate from this is reduced, with "hydrosulphite", a further and bigger precipitate of chromium hydroxide results. Analyses indicate 1,1/3 atoms of chromium to a molecule of dyestuff and the complex is therefore represented by formula VII.

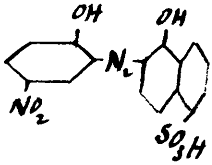


VI

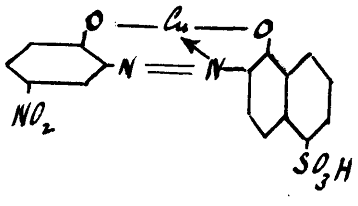


VII

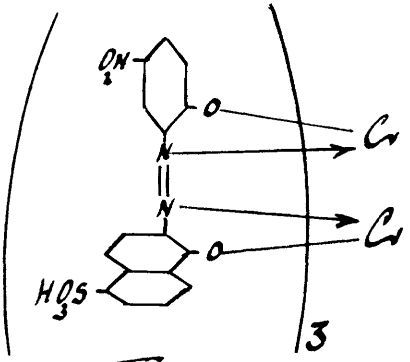
2-Hydroxy-5-nitrobenzeneazo-1-naphthol-5-sulphonic acid.



This dyestuff is an A-Naphthol derivative and so differs from any previously mentioned in this report. The copper derivative was prepared by adding copper acetate to an aqueous solution of the dyestuff, the lake being precipitated gradually. On testing, it was found that copper was present in the complex but not in the ionised state. One molecule of the dye had combined with an atom of copper and the complex is therefore represented by formula VIII. The chromium complex was obtained using chromium formate in a manner similar to that for the previous complex. It is soluble in water but contains no ionised chromium. There are 2/3 atom of chromium to a molecule of the dye. Formula IX.



VIII



IX

There is no evident explanation why the sulphonic acid group in each of the above compounds should have remained uncombined with metal.

The results of these investigations with o:o'-dihydroxyazo compounds indicate that in general metalisation results in the formation of typical inner complexes, both hydroxyl groups acting as acidic groups and either one or both of the azo nitrogen atoms co-ordinating with the metal. But, as has already been pointed out in the chapter dealing with the patent literature, some statements are made concerning these metallic lakes which cannot be explained by this theory of their nature. It should therefore form an interesting experiment to compare a commercially prepared metallic derivative with the corresponding derivative obtained by one of the above methods. The chief difficulty here is to determine the intermediates from which a given dyestuff of this class has been prepared. As far as the writer has been able to ascertain only the following dyestuffs of this class have been identified :- 1.Chlorantine Fast Rubine RLL. Fierz-David and Matter (J.S.D.C.53(1937) 432) give a formula which shows this colour to be the copper derivative of a di-o:o'dihydroxyazo compound.

2. Palatine Fast Blue G.C.N. (J.S.D.C.Abstracts.54(1938)138) is the chromium derivative of 2-naphthol-1-amino-6-sulphonic acid→ 1-naphthol-8-sulphonic acid.

3. Neolan Blue B is the chromium derivative of 1-amino-2-naphthol-4-sulphonic acid→2-naphthol (Mayer.Chemie der Organischen Farbstoffe. page 51)

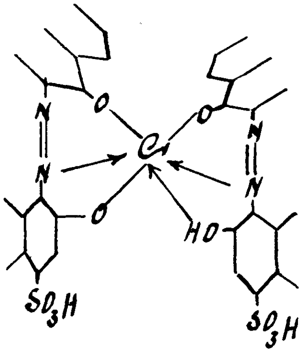
4. Neolan Blue G is the chromium derivative of 1-amino-2-naphthol-4-sulphonic acid→1-naphthol(Fierz-David. Kunstliche Organische Farbstoffe, Supplement page 47). It was decided to use this dyestuff for the experiment.

<u>1-Amino-2-naphthol-4-sulphonic acid→1-naphthol is</u> No. 201 in the Colour Index and that brand of it manufactured by the Society of Chemical Industry in Basle (the makers of Neolan Blue G) is called Chrome Fast Cyanine. This colour, when purified and boiled with chromium acetate, gave a chromium derivative which could be salted out - though its extreme solubility made salting out difficult. Analyses indicated that this product had ½ atom of chromium per molecule of dyestuff. Formula X.

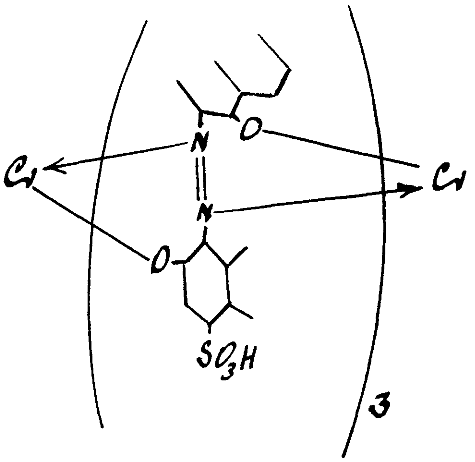
Eriochrome Blue Black B is also No.201 in the Colour Index, but is made by a different firm. Some of this/

/this was purified and boiled with chromium acetate, this time in acetic acid solution. The metallic derivative was salted out - more easily than the previous one - and on analysés was found to have 2/3 atom of chromium per molecule of dyestuff. Formula XI.

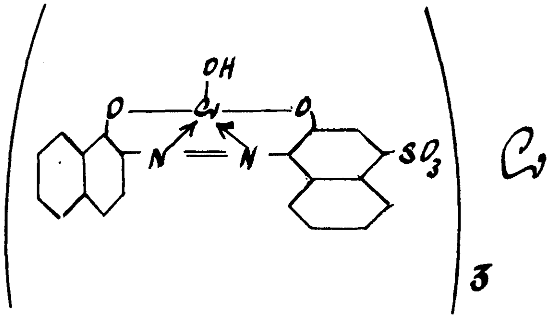
Next, Neolan Blue G was purified and when analysed was shown to have 1,1/3 atoms of chromium per molecule of dyestuff. Formula XII.



X



XI

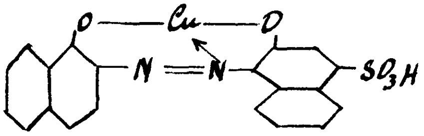


XII

Formula X was suggested by a formula given by Brass (Ber.68B (1935)1905) to the chrome lake of a salicylic acid azo dye in which he found one atom of chromium per two molecules. Formula XI is of a type which has been shown to be common among these products and the same can be said of XII. Formula XII makes Neolan Blue G the chromium salt of a chrome complex whereas it is generally assumed that such colours are sodium salts of the inner complexes, their solubility being due to the alkali salt portion and their fastness properties to the inner complex. Neolan Blue G was extremely soluble and yet the presence of ionised chromium was confirmed by qualitative tests. Assuming the Colour Index to be reliable in its identification of Chrome Fast Cyanine and Eriochrome Blue Black B and Fierz-David's account of Neolan Blue G to be correct, the above results prove that several chromium complexes can be prepared from one dyestuff. This confirms the statements to this effect which occur in the latent literature (e.g.B.P.364147,see page12). This point does not seem to have attracted investigators at all, though obviously of importance.

While these experiments were being conducted the copper derivative of Chrome Fast Cyanine was also prepared, by boiling the dye with copper sulphate, and was found to contain/

/contain one atom of copper per molecule of dye. Formula XIII.



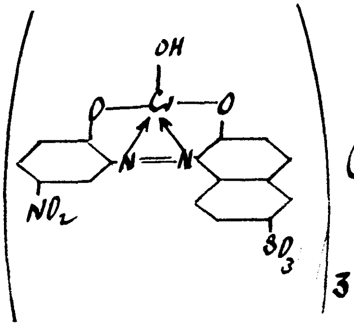
XIII

These derivatives are soluble in water and alcohol but insoluble in benzene.

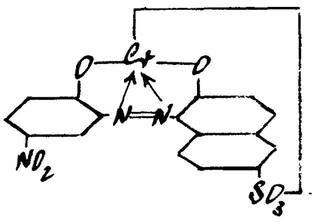
Primary and Secondary Chrome Complexes. These two classes of metallic derivatives differ, according to the patent literature (see page 15), quite widely in their dyeing properties and in the proportion of metal which they contain. It was decided to prepare a "primary" complex, convert it into a "secondary" complex and compare these two products.

The chromium derivative of 2-hydroxy-5-nitrobenzene-azo-B-naphthol-6-sulphonic acid was prepared by refluxing the dye with chromium formate as described on page 48. According to B.P. 446820 such a procedure gives a primary complex. Some of this product was heated in a sealed tube with hydrochloric acid, concentrations being similar to those given in the above patent, and the product isolated. Analyses showed that the primary compound had 1,1/3 atoms of chromium per molecule and the secondary had 1 atom of/

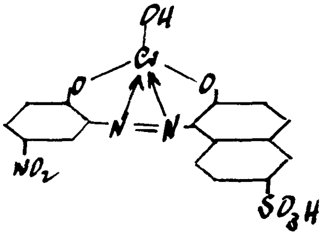
/of chromium. These results indicate that the compounds probably have formulae XIV and XV. respectively.



XIV



XV



XVI

The reactions of the primary and secondary compounds with acid and alkali are quite different. The secondary compound gives a red-violet solution in water which does not change on the addition of dilute hydrochloric acid, ammonia or sodium carbonate solutions. The primary compound gives a deep blue precipitate with acid (Patents claim that primary compounds are more sensitive to acid) and with alkalies there is a slow change of colour from red to deep blue. Some of the free colour acid of the primary compound (formula XVI) was prepared and it was found to give a deep red solution in water which changed slowly to deep/

/deep blue when ammonium hydroxide was added.

	Water	HCl	NH_4OH	Na_2CO_3
Primary	Red	Deep Blue Ppt.	Deep Blue Slowly	Deep Blue Slowly
Secondary	←	—	Reddish Violet	→
Free Acid	Deep Red	—	Deep Blue Slowly	No Action

The above table summarises the reactions in solution of these derivatives. These results imply that the secondary compound is not merely the free acid of the primary. They suggest that, though the free sulphonic acid of the complex may be first formed in the conversion of primary to secondary complexes, the sulphonic acid group combines with the monobasic chromium complex group to give an inner salt. Further that chromium in such combination with a sulphonic acid group is more firmly held than it is in the usual form of a chromium sulphonate; this being due to the implication already of the metal in a chelate ring. Thus there is formed a metallic complex in which the metal is linked to the organic residue at five points, that is, a quinquidentate compound. The combination between the sulphonic acid group and the metal must be of a different nature from that occurring in the primary compound since the/

/the secondary compound gives no precipitate of the colour acid with hydrochloric and (nor of chromium hydroxide with ammonia as is given by the primary). According to Diehl (Chem.Revs.21(1937), 40) no quinquidentate chelate compounds have been recorded. Secondary compounds, such as the above, seem however, to merit the description "quinquidentate" and if so they constitute a new development in the study of chelation.

o-Alkyloxy-o-Hydroxyazo Compounds.

B.P.292,660; 296819; 395,968 deal with the preparation of metallic derivatives of o-alkyloxy-o-hydroxyazo compounds. The reaction is done under conditions such that the alkyloxy group is converted to a hydroxyl. The method is used for those dyestuffs whose alkyloxy compounds when diazotised have a coupling capacity superior to the diazotised hydroxy compound. Thus better yields of the compounds are obtained. B.P.296819 states that o-hydroxy monoazo dyes which contain an o-alkyloxy group instead of a hydroxyl, when treated with metallic compounds may give metallic complexes. Conditions favourable to splitting off the alkyl group are obtained by heating aqueous solutions under pressure at temperatures above 100° C., or in some cases prolonged boiling under a reflux is sufficient. The same products are obtained as when o-hydroxy monoazo dyes which are not substituted are used. The patent says the most suitable conditions must be ascertained by trial in each case. B.P. 395,968 advocates heating with chromic sulphate for chrome complexes at some temperature, depending on the particular dyestuff, between 110° C. and 150° C.; the most generally applicable range being/

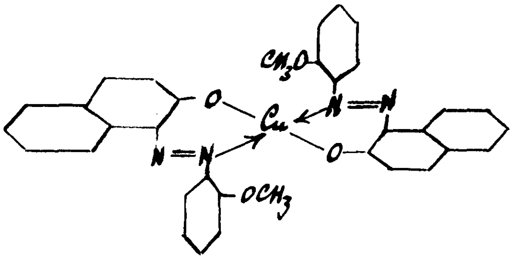
/being between 130° C. and 140° C.

To investigate this, the azo compound from o-anisidine B-naphthol (Colour Index 113) was prepared and purified.

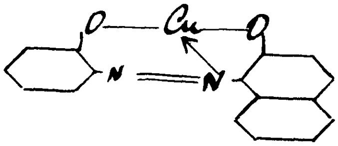
Copper Derivatives. Alcoholic solutions of the azo compound and copper acetate were refluxed together and the copper complex separated by adding water. It is a red-brown powder almost insoluble in water but soluble in alcohol and is dissociated by heat. Analyses indicate that one atom of copper has combined with two molecules of the dye and it is represented by formula I which shows the methoxyl group unchanged.

The experiment was then repeated under pressure, the alcoholic solutions being heated at 130° C. for four hours. Two products were obtained in this way, the first (constituting over 90% of the total yield) was a green colour and sparingly soluble in alcohol while the second appeared to be identical with the compound already described (Formula I). The former was a new compound containing one atom of copper per molecule of azo compound. Treatment under pressure has in this case hydrolysed the methoxyl group and given a compound having/

/having formula II.



I

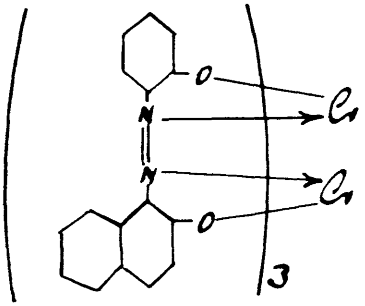


II

The second compound is unaffected by alkalies while the first is broken down by them to copper hydroxide and the original dye. Formula I represents a co-ordinatively saturated (see **page 36**) compound but in II the metal has still a free co-ordinate valency. The comparative ease with which this compound can be purified enables one to conclude from the analytical results that this free valency has not been used to attach a molecule of the solvent to the metal and that the compound is co-ordinatively unsaturated therefore.

<u>Chromium Derivative</u>. Alcoholic solutions of the azo dye and chromium formate were refluxed together but no combination took place. When heated at 130° C under pressure however, a dark blue compound, insoluble in water but/

/but soluble in alcohol was obtained. This compound contained 2/3, atom of chromium per molecule of the dye (Formula III). The chromium could be precipitated by the addition of ammonia to an alcoholic solution of the derivative, indicating that this compound is not very stable.



III

From this it appears that treatment under pressure has three distinct effects :-

1. Since no combination took place when the solutions were merely refluxed, pressure treatment facilitates complex formation between the metal and hydroxyl group.
2. It converts the methoxyl to a hydroxyl.
3. Since all the valencies of the metal have been used by the organic molecule - no basic hydroxyl group remaining, as sometimes happens with chromium complexes (see page 46,47 etc) treatment under pressure appears to encourage the maximum saturation of dyestuff with the metal.

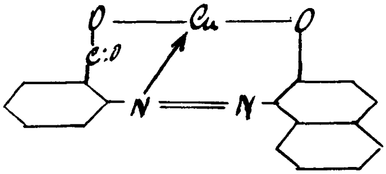
These experiments confirm the claims in patent literature that o-alkyloxy compounds give metallic derivatives, if the conditions of the reaction are such as first to hydrolyse the alkyloxy group. Such reactions do not seem to have been investigated or recorded in the chemical literature. The copper derivatives also make an interesting comparison of mono-and di-o-hydroxy lakes that are closely related and show conclusively that in the latter both hydroxyl groups take part (see page 30).

Since this work was done, Drew and Landquist (see page 29) have prepared the copper derivatives of o-hydroxy-benzeneazo-B-naphthol and given it the same formula as II.

o-Carboxyl-o-Hydroxyazo Compounds.

B.P. 116530 deals with the copper compounds of dyestuffs prepared from o-diazo-carboxylic acids. A carboxyl group o- to the azo link has long been known to confer mordant dyeing properties. It was decided to attempt the preparation of such a lake and for this purpose the azo compound from anthranilic acid ⟶ B-naphthol (Colour Index 214) was prepared.

Copper Derivative. The copper derivative was prepared by refluxing alcoholic solutions of the dye and copper acetate, and filtering off the product. It is a red-brown powder, slightly soluble in alcohol and insoluble in water, and is liable to be contaminated with basic copper salts. These impurities can be removed by boiling with dilute acetic acid. The copper can be precipitated from an alcoholic solution of the lake by the usual reagents, such as sulphuretted hydrogen. On analyses it was found to have 1 atom of copper per molecule which suggests formula I.

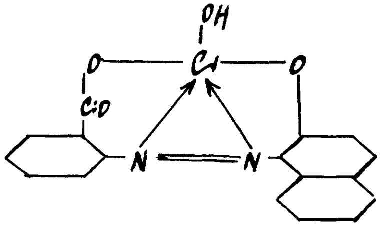


I

Since this experiment was made, an account of the above derivative has appeared (Drew and Landquist see page 29) in which it is shown by analogy with the copper compound of salicylidenanthranilic acid that the nitrogen which is co-ordinatively linked to the metal is probably that one nearest to the carboxyl group. By molecular weight determination they excluded the possibility of a dimeric structure and they also showed that m- and p-azo-carboxylic acids behave quite differently from the above.

This derivative was also prepared by boiling an aqueous suspension of the dye with cuprammonium sulphate. The product was however largely contaminated with the free dyestuff and basic copper salts.

Chromium Derivative. Alcoholic solutions of the azo compound and chromium formate were refluxed together and the chromium derivative precipitated by adding water. It is a red powder, soluble in alcohol but insoluble in water containing 1 atom of chromium per molecule of dye formula II.

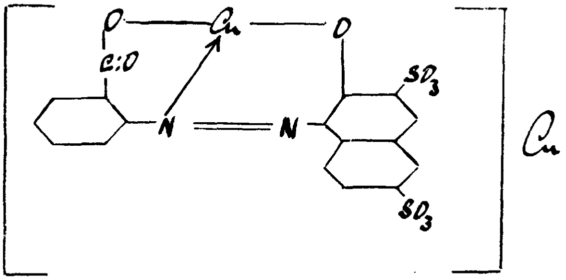


Unlike the copper derivative, the metal in this compound is firmly held. This is shown by the fact that it can be prepared in glacial acetic acid solution and will withstand boiling in this reagent even longer than will the original azo body. This was shown by boiling a solution in glacial acetic acid of the azo compound and chromium acetate. Combination took place and the chrome complex could be precipitated by the addition of water. The heating was continued and eventually some of the original dyestuff in excess was decomposed into B-naphthol and a tarry residue while the complex was still intact.

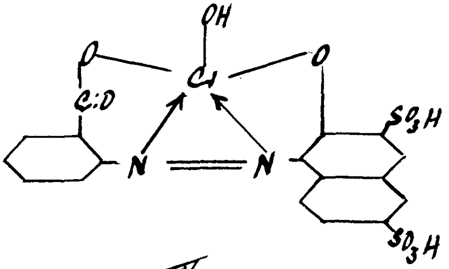
The above example of this class of azo mordant dyestuff is of only theoretical interest. Its sulphonic acid derivatives are more interesting from a technical standpoint. Their extreme solubility however, makes their examination and preparation much more difficult. But it was thought worth while to attempt the investigation of the copper and chromium derivatives of a typical member of this series of colours. To this end the commercial dyestuff <u>Solochrome Red B</u> (Colour Index 216.Anthranilic acid⟶2-naphthol-3:6-disulphonic acid was purified.

Copper Derivative. This was prepared by boiling an aqueous solution of the dye with copper acetate. It is a brown-red powder, soluble in water, slightly soluble in alcohol and insoluble in benzene. A solution of it gives no indication of copper with alkali but does with hydrogen sulphide. After reduction with "hydrosulphite" however, all the copper is precipitated. Analyses indicate 2 atoms of copper per molecule (Formula III).

III



Chromium Derivative. This was prepared by boiling an aqueous solution of the dye with chromium acetate. The resulting compound was extremely soluble, so its free acid was precipitated by adding dilute sulphuric acid. This is a red powder giving a red solution in water. It contains one atom of chromium per molecule and is stable to boiling dilute sulphuric acid and ammonia (Formula IV).

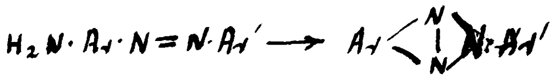


IV

The properties of the copper derivatives of the two azo bodies described above, point to the conclusion that an o-carboxyl group, though it resembles an o-hydroxyl, results in the formation of a less stable link between the azo compound and the metal. Since this effect is not apparent in the chromium derivatives, it follows that the substitution, in the o-position to the azo link, of a carboxyl for a hydroxy group does not reduce to a great extent the lake forming power of the azo compound.

o-Amino-Azo Compounds.

Crippa (Gazz. Chim.Ital.55,706(1925)) states that when o-aminoazo compounds are boiled in aniline (which acts as an oxidising agent) with iron or copper powder, ring closure takes place with the formation of triazoles :-



(Ar and Ar' are any aromatic nuclei)
Later, the same worker tried to use nickel and cobalt as catalysts, instead of iron and copper which were not entirely satisfactory, and found that these led to metallic organic compounds of the composition A_2 M. (where A is the azo derivative). These metallic derivatives are stable to alkalies but decomposed by dilute acid. He claims that o-hydroxy-o-aminoazo compounds of the benzene series do not give these metallic derivatives.

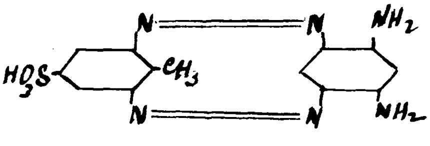
Charrier and Beretta (Gazz.Chim.Ital.56,865(1926)) prepared the copper derivative of benzeneazo-B-naphthylamine, which contains one atom of copper to two molecules of azo compound, by boiling the azo compound with copper sulphate and ammonia in aqueous alcoholic solution. This derivative is stable to alkalies but decomposed by dilute acids. They suggest that the formation of metallic compounds is an intermediate stage/

/stage in the production of triazoles from o-aminoazo bodies.

Pfeiffer (Jour.pr.Chem.149,Oct.1937) claims that o-aminoazo compounds give inner complex salts just as do o-hydroxyazo compounds. The cobalt derivative of benzeneazo-B-naphthylamine contains one atom of cobalt to three molecules of the azo body, but benzeneazo-B-naphthylamine-4-sulphonic acid when treated with ammoniacal copper sulphate gives a triazòl.

In the patent literature, the copper and chromium complexes of o-amino-o-hydroxyazo dyes are often mentioned as giving valuable dyestuffs. As a preliminary to investigating this, it was therefore decided to attempt the preparation of the copper and chromium complexes of an o-aminoazo dyestuff. It was also anticipated that the results would be interesting in the light of the work described above.

Toluylene Brown G. (Colour Index 333).

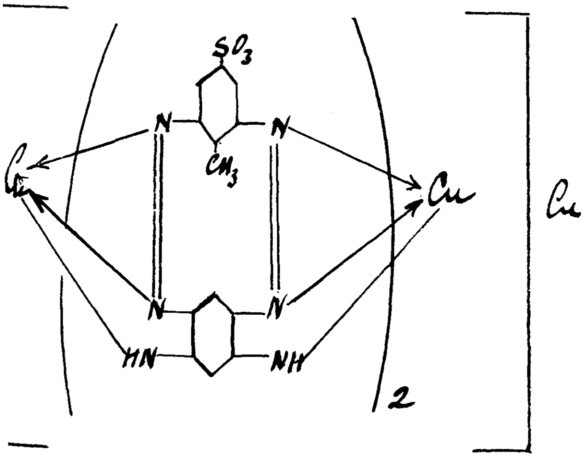


Since this colour contains two azo links with an amino-o- to each, it might be considered as equivalent, for experimental purposes, to an aminoazo compound with one amino group o-to the azo link.

<u>Copper Derivative</u>. This was prepared by refluxing the dyestuff for some hours with copper acetate, in aqueous solution. On evaporation a brown powder was obtained which was stable to alkali but contained copper in a complex state. No tendency was apparent for the reaction to continue further with the formation of a triazol Analyses indicate that it contains 1.5 atoms of copper per molecule. Formula I.

<u>Chromium Derivative</u>. This was prepared by refluxing the dye for some hours with chromium acetate. This compound was purified by boiling with dilute acetic acid - which would also remove any chromium that might be in the sulphonic acid group. It was found to be insoluble in water, stable to alkali - giving a more soluble salt - and decomposed by dilute mineral acid.

The metal is in a complex form and analyses indicate 2/3 atom of chromium per molecule Formula II.



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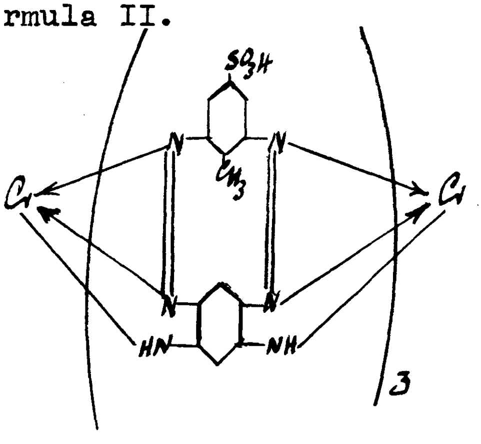
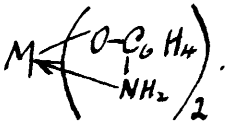


II

These results lead to the conclusion that an amino group o-to the azo link acts similarly to an hydroxyl group, i.e. by hydrogen displacement it can combine with copper or chromium, forming part of a chelate group. Metallisation took place in both cases, without difficulty and there were no signs of triazol formation.

Metallic Derivatives of o-Aminophenols.

Horn (Jour.pr.Chem.149,298(1937)) states that o-aminophenol gives a very soluble copper compound of formula $(H_2N.C_6H_4O)_2Cu$ which becomes almost insoluble in water, alcohol or other organic solvents when heated. He suggests this is due to a change into an inner complex salt. Huber and Schnackig (Z.anorg.Chem.226,209(1936)) say there is probably formed first a compound having such a formula as $X_2M(H_2N.C_6H_4OH)_2$ - where MX_2 is the original metallic salt used in the preparation - and this then loses 2HX to give a compound of the general type



$$M\left(\begin{array}{l}-O-C_6H_4\\ \leftarrow NH_2\end{array}\right)_2.$$

As has already been mentioned (page 10), the patent literature mentions the practicability of preparing the metallic derivatives of o-aminophenols and naphthols and using these to prepare dyestuffs known as "half-chrome compounds", but it does not distinguish between the two classes of metallic derivatives available from o-aminophenols.

A comparison of such metallic derivatives with those from o-substituted azo dyestuffs should be interesting, since the above information indicates that, in their final stage at least, the metal is part of a chelate ring, and the/

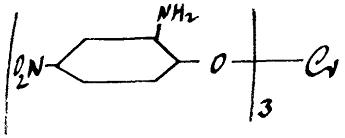
/the products must be true inner complex compounds.

The copper derivative of <u>o-aminophenol</u> was prepared by refluxing the organic compound with copper acetate. A grey-black product was obtained which was insoluble in water and decomposed by dilute acid. It is slightly soluble in alcohol and the metal can be removed by adding alkali. An attempt was made to diazotise this derivative but without success, since the copper was so insecurely held.

B.P. 15456/15 says that when 4:2:1-nitroaminophenol is boiled with a chromic salt, there is formed an easily soluble chromium compound. This compound can be diazotised and coupled in the usual way. An attempt was made to prepare this product by boiling the nitroaminophenol with chromium formate. A brown red chromium derivative was obtained which was insoluble in water. By salting out the filtrate there was obtained little more than a trace of a yellow chromium derivative. This latter compound may be the same as that mentioned in B.P. 15456/15 but there was not enough to investigate it further.

Since the yield of the brown-red insoluble compound is almost quantitative, it appears that this patent does not/

/not give all the relevant details for the satisfactory preparation of a soluble chromium derivative. The properties of the insoluble derivative were quite different from those of the derivative described in the patent. The former is insoluble in water, alcohol, ether or benzene. The metal is split off by dilute acids and consequently the compound cannot be diazotised in the usual way. Analyses indicated that it contained 1/3 atom of chromium per molecule. Formula III.



III

These properties suggest that this compound is not an inner complex, while the description of the soluble yellow compound given in the patent literature indicates that in the latter the metal is in a complex union. This is not in agreement with the accounts of Horn and Huber etc. (ibid) who hold that the water insoluble derivatives are the complexes.

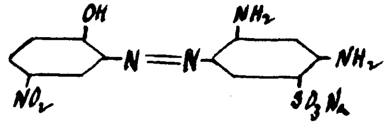
A similar result was obtained when 4:2:1-nitroaminophenol was boiled with copper acetate. Two compounds were obtained, one in large yield which was insoluble and a small amount of a soluble compound.

The investigation of these metallic derivatives of o-aminophenols was not carried further, since it was related only indirectly to the subject of the research.

o-Amino-o-Hydroxyazo Compounds.

It has long been known that an amino group o- to the azo link conferred mordant dyeing properties and patents e.g. B.P. 210890, have dealt with the preparation of soluble copper and chromium derivatives of o-amino-o-hydroxy azo dyestuffs. Morgan and Main Smith (see page 27) prepared the cobalt lake of Metachrome Brown B and came to the conclusion that the amino group took no part in the complex formation. The work already described here under the o-aminoazo compounds shows that their conclusion is probably unfounded and that an amino group o- to an azo link reacts in exactly the same way as an hydroxyl group. It is possible however, that when they are both o- to the same azo link, the hydroxyl group might in some way prevent the amino group from the taking part in the chelate ring. It might, for instance, combine preferentially with the metal. To investigate this possibility it was decided to prepare the copper and chromium derivatives of an o-amino-o-hydroxy-azo dyestuff.

Chrome Brown T.V. (Colour Index 98)

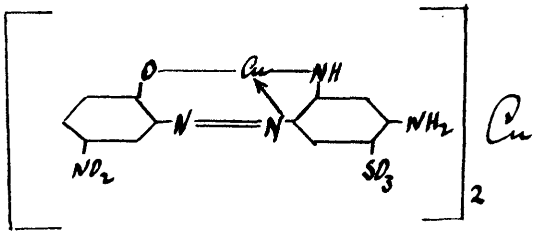


The copper compound was prepared by boiling an aqueous/

/aqueous-alcoholic solution of the dyestuff and copper acetate. It is a dark brown powder soluble in water but insoluble in alcohol or benzene. When acid is added to the solution, a precipitate of the free colour acid is obtained and some copper is removed from the dye. The colour acid gives a clear red solution in alkalies. On reduction with "hydrosulphite", the compound is broken down and the copper which was in complex combination precipitated. Analyses indicate that there are $1\frac{1}{2}$ atoms of copper per molecule. Formula I.

The chromium compound was prepared by boiling the dyestuff with chromium formate in aqueous solution. It is a red brown powder, slightly soluble in water, insoluble in organic solvents. Some of the chromium content is removed by alkalies but most is in the form of a complex and to remove this, the azo link has to be broken. The free colour acid of the chromium complex is more soluble than its chromium salt. The complex is not broken down, either wholly or in part, by dilute acid. Analyses indicate that there is 1 atom of chromium per/

/per molecule of dyestuff. Formula II.



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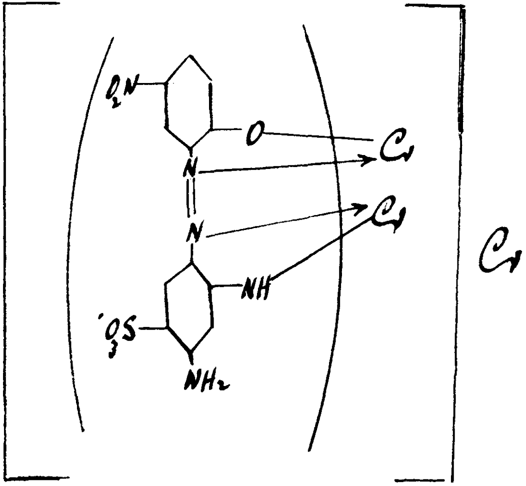


II

These results point to the conclusion that in o-amino-o-hydroxyazo dyestuffs, the o-amino group reacts in the same way as the o-hydroxy and does not cause any obvious decrease in the stability of the complex. It is also interesting to note that the amino group in the para position to the azo link does not appear to participate in the reaction.

The above complexes show that the statement by Crippa (see page 68), that o-amino-o-hydroxyazo compounds of the benzene series do not give metallic complexes, is not strictly accurate.

Preparation of Metallic Derivatives of Dyestuffs by Electrolysis.

From what has already been written it will be clear that the metallic derivatives of o-substituted azo compounds contain the metal combined with the azo body as part of an inner ring. In this complex form the metal is un-ionised. This is shown by the partial or complete inhibition of the analytical tests for the metallic ions. For this reason, it occurred to the writer that it might be possible to prepare these compounds satisfactorily by electrolysis.

Considering the copper derivatives: if two plates of copper are used as electrodes and a solution of the dyestuff to be metallised as electrolyte, then when a current is passed cupric ions would be expected to travel through the solution. These ions would be taken up, in passing, by the dyestuff to form the copper complex and so the concentration of cupric ions in solution would be kept at nil, or at least very low. This process would probably continue till all the complex forming groups had been saturated with the metal and then copper taken from the anode would be deposited in the usual way on the cathode.

If this reaction could be brought about, it would be not only a method of preparation but, at the same time, would give a direct means of measuring the ratio of metal to dyestuff in the complex compound formed; for it would seem to be an easy matter to determine the weight of copper which was lost by the electrodes and the quantity of dyestuff, used in the first place, which had been saturated by this amount of metal. But when attempts were made to apply this method of preparation there were found to be many difficulties which could not be easily overcome and it was thought inadvisable to spend much time on the problem.

The first difficulty encountered was that the products of the reaction settled on the surfaces of the electrodes. This meant that the electrodes had to be separated from the solution of the dyestuff. Porous pots containing water were immersed in the solution and the electrodes suspended in the pots. The product of the reaction, however, settled on the pots and no doubt to some extent within their walls, causing a very high resistance to the passage of current. Another method used was to connect three beakers by two gelatine bridges. In the first beaker containing the anode, was a solution of copper sulphate of/

/of known strength; in the second was the solution of the dyestuff and in the third, which was the cathode compartment, was a very dilute solution of sulphuric acid. To reduce the resistance of the bridges, copper sulphate solution was mixed with the gelatine. Despite the cooling effect of an ice jacket round each beaker, the heating effect of the current was sufficient to melt the gelatine and so prevent this device from being very satisfactory.

The dyestuffs used for the experiments were the sodium salts of o-hydroxy-azo-sulphonic acids. The free acids could not be used because of their insolubility. In no instance could the method be made to work in anything approaching a quantitative way and it was even impossible to obtain sufficient of the reaction products for analyses, due to the limited amount of dyestuff which could be accommodated in the apparatus. The nature of the products had therefore to be deduced from qualitative experiments. Orange II, Crystal Scarlet and Ponceau 4 G.B. were investigated. Each gave a derivative of the dyestuff containing both ionised and un-ionised copper, indicating the combination of the metal with the sulphonic acid group or/

/or groups and also its presence in an inner complex ring. The dyeing property on wool of the derivative from Ponceau 4 G.B. was compared with that of the dyestuff itself and that of its copper complex prepared as on page 39. The electrolytic product was found to give a fast colour, much darker than that of the original dye though not quite so dark as the chemically prepared copper complex. This indicated that the electrolytic treatment had not fully saturated the azo compound with metal, though it had given an internal complex compound.

In this method, the chief difficulty lies in finding a way of separating the electrodes from the electrolyte and still maintaining a reasonably low resistance for the circuit. If this could be overcome, some interesting results might be obtained.

Basicity of Chromium in Complexes.

In many of the compounds described in this research, an hydroxyl group has been shown combined with chromium while the latter is part of an inner complex. (pages 47, 52, 55, 64, 66). Similar formulae have appeared in the literature (Kopp.Bull.Soc.Ind.Rouen.1935; Brass,Ber. 68B,1935; Ender and Muller, Milliand.Textilber.1938) but no proof of the existence of an hydroxyl group in such compounds has been seen by the present writer. Therefore it seemed desirable to obtain some experimental evidence either for or against the existence of basic chromium in these inner complex compounds.

Magnesium ethyl iodide was added to the chromium derivative of anthranilic acid→B-naphthol (page 64). There was a brisk evolution of gas which was collected in a nitrometer and on analysis proved to be ethane. All the reagents and apparatus had been carefully dried and the reaction was soon completed, no more gas being evolved after about fifteen minutes.

This experiment seemed to prove in a qualitative way that the chromium complex of anthranilic acid→B-naphthol/

/B-naphthol contained an hydroxyl group and so confirms the interpretation of the analytical results which shows the metal in the complex ring to be basic. It is reasonable to extend this confirmation to the other derivatives which have been represented as containing chromium in a similar state.

Analytical Methods.

The literature dealing with methods of analysis suitable for this type of metallic lake seems to be rather meagre, so it may be useful to record the methods which were found to be most satisfactory by the present writer.

Copper. The simplest way to detect copper in such compounds is to ash the derivative, dissolve the ash in acid and test for copper ions in any of the usual ways. Alternatively, if the compound is soluble in water, any ionised copper can be precipitated by the addition of alkali. "Hydrosulphite" is then added to the filtrate to break up the dyestuff molecule and any copper that may have been in complex union appears as a precipitate of copper "sulphide", which can be easily identified.

For the quantitative estimation of copper, the following three methods were found to be satisfactory.

(1) Ash the compound, dissolve the copper oxide in boiling dilute nitric acid and titrate with thiosulphate according to the customary procedure. This is undoubtedly the simplest way but many of these derivatives deflagrate on/

/on heating so that it is not applicable, while others swell to such an extent as to overflow from the crucible. In the latter case addition of ammonium nitrate is sometimes helpful.

(2) When sulphur in a complex was estimated by a peroxide fusion, the residue after thorough extraction with boiling water, consisted of copper oxide and iron (from the crucible). This residue was taken up in dilute hydrochloric acid and hydrogen sulphide passed through the solution; the copper sulphide allowed to settle; filtered off and dissolved in dilute nitric acid. A thiosulphate titration gives the amount of copper in this solution.

(3) Prolonged heating of these complexes with conc. sulphuric acid can be used as the basis of an analytical method when neither of the above is suitable or convenient. 0.2 to 0.5 grams of the metallic derivative is heated in a Kjeldhal flask with 7 c.c conc. sulphuric. (By adding a little of the selenium catalyst used in Kjeldhal estimations of nitrogen, the period required to oxidise the organic matter can be reduced from about 6 to 3 hours). When all the carbonaceous/

/carbonaceous matter has been destroyed and the contents of the flask are cold, the solution is poured into a beaker, diluted, and almost neutralised with sodium carbonate (about 10 grams). The copper is precipitated from this solution by adding some strips of aluminium and boiling till the solution is colourless (about 1 hour). Remove the aluminium, washing off any adhering copper by a jet of water into the beaker. Decant the supernatant liquor through a filter paper and any small amount of copper on the paper can be returned to the main residue of metal by dissolving in dilute nitric acid. Dissolve the copper in dilute nitric acid. (Any signs of a selenium residue is filtered off at this stage). The solution of copper nitrate is then boiled with urea to remove nitrous acid, according to the usual procedure, neutralised with sodium carbonate, made acid with acetic acid and titrated with thiosulphate.

The reason why the copper sulphate solution, obtained after the oxidation of carbonaceous matter, cannot be prepared for titration with thiosulphate without removing the copper, is that the present writer has found the large amount of sodium sulphate (formed by/

/by neutralising the sulphuric acid) vitiates the starch-iodine end point in the thiosulphate titration. The above procedure has been found, in this research, to be the most satisfactory way of overcoming this obstacle.

Chromium. Chromium in these compounds may be detected either by ashing the derivative or, if soluble in water, by reducing the dyestuff with "hydrosulphite"; then converting the precipitated chromium hydroxide into a chromite by dissolving in excess alkali. The chromite solution is then oxidised to a chromate by hydrogen peroxide; excess oxygen boiled off; acidified with acetic acid and chromate detected in the usual way as barium or lead chromate.

Two suitable methods for the quantitative estimation of chromium in these metallic derivatives are :-

(1) 0.2 - 0.3 grams of the complex is ashed in a porcelain crucible. The ash is fused for 10 minutes with 2 parts sodium carbonate and 1 part potassium nitrate. Extract with boiling water. Acidify with hydrochloric acid. Boil with urea to remove any nitrate. Since some of the/

/the bichromate may be reduced by the boiling in acid solution, it is necessary, by adding excess alkali, to convert any chromic salt to chromite and then to oxidise this to chromate by boiling with hydrogen peroxide. When all the oxygen has been driven off, the solution is cooled, neutralised and acidified with hydrochloric acid (at least 10 ml.conc. per 100 ml. solution, or final titration figure may be too high). The chromium can then be estimated by titration with thiosulphate and potassium iodide in the usual way.

(2) The complex may be fused with sodium peroxide, as in a sulphur estimation (q.v.); the melt extracted with boiling water and boiled with more peroxide (sodium or hydrogen) to precipitate any iron (from the crucible) in solution as ferrate. When all the oxygen has been driven off, filter to remove any precipitated iron; acidify and titrate with iodine and thiosulphate. It is advisable to add a little sodium fluoride before titrating to prevent any iron that may still be in the solution from causing a high result.

Sulphur.

Sulphur was estimated by the usual fusion method, using sodium peroxide and sodium carbonate. After extraction and filtration of the melt, it was usually found that there was a little iron in the filtrate - either in a colloidal state or as ferrate. In order to precipitate this iron with the rest, a little sodium peroxide was added to the extract from the crucible and boiled for 10 minutes.

On one occasion an attempt was made to estimate the sulphur in a chromium complex (from p-nitro-o-aminophenol → Schaffer's Acid. See page 48) by the Carius method. The method was unsatisfactory because most of the sulphur appeared to have combined with the chromium to give a compound which was insoluble in a dilute acid solution. When the Carius tube was opened after the reaction and the dark green liquid therein diluted, a pale amorphous precipitate was obtained. Only about 1/5 of the actual amount of sulphur present in the complex was obtained by the action of barium chloride on the filtrate from this. On ashing this precipitate, the indications were that it was an inorganic derivative of chromium, presumably/

/presumably containing the remainder of the sulphur. Its exact nature was never established.

Nitrogen.

Since these compounds are, in general very difficult to combust, the Dumas estimation of nitrogen would probably be inadvisable. On several occasions, however, the method was used on the hemi-macro scale and under these conditions found to be reasonably satisfactory. As would be expected, the only difficulties that arose were connected with the length of time required for the combustion which varied, from $\frac{3}{4}$ to 2 hours, depending on the nature of the complex.

Morgan and Main Smith (J.C.S.120,1728) using cobalt lakes found that the Kjeldhal method was applicable, if the complexes were first reduced with "hydrosulphite". The present writer, however, found it more satisfactory to follow the considerably modified Kjeldhal scheme given in Bull.Soc.Chim.45,312(1929). Briefly, this consists in reducing the dyestuff in an aqueous-alcoholic medium with "hydrosulphite"; adding conc. sulphuric acid and heating to drive off alcohol; then continuing according to the usual/

/usual Kjeldhal procedure. The main difficulty here lies in the excessive frothing which often accompanies the driving off of the alcohol. The care necessary at this stage makes the method long and tedious. Some time can be saved later by using the selenium catalyst, instead of the proposed copper sulphate.

Calculation.

Since most of these complexes can be obtained in the 100% pure condition only with great difficulty, it was decided to base the interpretation of the analytical results upon the ratio between the amount of metal present and the amount of some constituent, such as sulphur or nitrogen, in the dyestuff molecule. This removed the necessity to purify the complexes from such innocuous materials as sodium chloride - though when sulphur was being estimated it was essential to ensure that no sodium sulphate was present. Many of the commercial dyestuffs used as starting materials contain a fair proportion of sodium sulphate.

In one or two cases where the complex could be easily obtained free from all impurities, only the metal present was estimated.

EXPERIMENTAL.

Mono-o-Hydroxyazo Compounds.

Benzene-azo-B-naphthol. M.W 248.

This colouring matter was prepared from aniline and B-naphthol in the usual way. It was purified by recrystallising from alcohol. The first method used to prepare the copper derivative of this compound, was to reflux a solution containing 4 grams copper sulphate with a suspension of 3 grams benzene-azo-B-naphthol in 500 mls. of water for six hours. The brown copper compound, so formed, was filtered off, washed with alcohol, then further purified by a Soxhlet extraction with alcohol. The product however was still contaminated with benzene-azo-B-naphthol and it was decided to prepare the lake by a reaction in which the parent colouring matter would be in solution.

Therefore, an alcoholic solution containing 5 grams benzene-azo-B-naphthol was refluxed with 1.6 grams copper chloride and 1.85 grams potassium acetate in alcoholic solution. The potassium acetate functioned as an acid binding agent. (It is noteworthy that copper sulphate reacted with an aqueous suspension of the azo body without need for an acid binding agent, whereas for the azo body and copper/

/copper chloride, both in alcoholic solution, to react, potassium acetate must be present). An insoluble brown copper compound was obtained, but again it was contaminated with the original azo compound.

A third attempt was made to prepare this compound in a pure state. The method was that used by Elkins and Hunter (J.C.S.(1935),1598). To a hot nearly saturated solution of benzene-azo-B-naphthol(1 mol.) in alcohol, was added a solution of copper acetate, (1 mol. excess) in 50% aqueous alcohol, dropwise. The copper complex was precipitated as a fine brown powder, which seemed much more colloidal than that obtained by the other methods of preparation. However when purified by extraction with toluene and washing with alcohol, it was analysed.

Found :- % N_2: 10.0; 10.1. % Cu : 10.5: 10.6.

∴ Nitrogen/Copper = 4/.93 atoms.

∴ Dye/Copper ratio is 2 mols/.93 atom.

p-Nitrobenzene-azo-B-naphthol. (Para Red) M.W 293.

The following method was found to be most suitable for the preparation of Para Red. It is taken from a handbook issued by a firm of dyemakers, the quantities having been suitably reduced. 14 grams parnitraniline dissolved in 60 mls. boiling water and 22 mls. conc. hydrochloric acid. This is then cooled with thorough stirring to give finely divided paranitraniline hydrochloride. Add 50 mls. cold water and 50 grams of ice, followed by the addition, all at once of 26 mls. sodium nitrite solution. (290 grams $NaNO_2$/litre). Then add 30 grams sodium acetate and dilute the whole to 500 mls. This diazo solution is added to a solution of 12.5 grams B-naphthol in 20 mls. sodium hydroxide (36^{o}Tw) which has been diluted to 500 mls.

After purification, 6 grams Para Red in aqueous suspension were refluxed with copper acetate solution for 8 hours. The insoluble brown compound was purified by extraction in a soxhlet with chloroform (which was found to be a better solvent for Para Red than toluene).

The copper in this complex (like the previous one) could not be estimated by simple ignition, due to/

/to volatilisation of the azo body which carried off some of the ash. Copper was therefore estimated according to method 3 page 86.

% Cu :- Found, 10.1; 10.1. Calculated 9.8.

Sulphanilic Acid ⟶ B-naphthol (Orange II) M.W. 328.

By boiling Orange II with copper chloride and sodium acetate, there is obtained a finely divided red-brown precipitate. The following method was found, however, to give a purer product. 1 part (by weight) Orange II (Commercial dyestuff was dissolved in water, filtered hot and allowed to deposit on cooling) was dissolved in 15 parts of water and to the warm solution was added a cuprammonium solution containing 1 part copper sulphate. A red-brown precipitate was formed. This was washed with weak ammonium hydroxide, water, alcohol and ether and dried in vacuum in presence of ammonium carbonate. These precautions in drying were taken because the compound lost ammonia when heated, and it was desired to estimate the ammonia in the compound. Copper was estimated by ignition, sulphur by fusion and ammonia by heating the complex with sodium hydroxide and collecting the ammonia evolved in standard acid. The method is not a very/

/very satisfactory one. It gives high results, probably due to some slight decomposition at the azo link. The results obtained, however, are indicative of the number of molecules of ammonia present per molecule of complex.

% Copper :- 13.4, 13.3. % Sulphur :- 7.40, 7.45.

∴ Sulphur/Copper = 1/.91. Dye/Copper = 1/.91.

%Ammonia:- 8.1, 8.3. Dye/Ammonia = 1/2.3

This compound was sparingly soluble in water and was sensitive to dilute acid. With alkali, some copper was removed and after reduction by "hydrosulphite" the remainder was precipitated.

Chromium Complex. As already described on page 40, an attempt was made to prepare the chromium complex of Orange II according to the method suggested by B.P. 104,045. Chromium hydroxide was precipitated from 3.5 grams chromium fluoride. 50 grams of 30% sodium hydroxide solution were added to the chromium hydroxide and the mixture heated, with stirring, to 60°C. Then a paste of 12.5 grams Orange II in 5 mls. of water was added; the whole heated to boiling for two hours; then diluted to 70 mls. and heated for a further 5 minutes. The excess chromium hydroxide was filtered off and from the filtrate unchanged Orange II was deposited, on standing.

The solution was acidified and a light brown compound salted out. When aqueous ammonia was added to a solution of this product, chromium hydroxide was precipitated, and on reduction of the resulting solution with "hydrosulphite" more chromium hydroxide was precipitated. This indicates that the product is a complex similar to the copper one but there was insufficient of it for analysis and the method does not seem, therefore, to be very satisfactory.

Aniline → B-Naphthol-6-sulphonic acid (Ponceau 4 G B) M.W. 328.

Commercial Ponceau 4 GB was purified by dissolving in water, filtering and precipitating from solution by alcohol. Aqueous solutions of the dyestuff and copper acetate were mixed. No precipitate was obtained in the cold but on warming, a finely divided dark brown copper complex was formed. It was purified by boiling with water and a little dilute aq. ammonia.

This derivative loses some of its copper content when treated with alkali in the cold. The copper in the complex is removed by boiling alkali. The complex is also broken up by dilute acids. As already stated on page 41, no precipitate is obtained with potassium ferrocyanide until the solution has stood for some considerable time. It is/

/is slightly soluble in water, alcohol and ether. Insoluble in benzene.

% Sulphur :- 7.93, 7.96.

$\therefore \frac{\text{Sulphur}}{\text{Copper}} = \frac{1}{.99}$ atoms.

% Copper :- 15.3, 15.4.

$\therefore \frac{\text{Dye}}{\text{Copper}} = \frac{1\ \text{mol.}}{.99\ \text{atoms.}}$

o:o'-Di-Hydroxyazo Compounds.

2-Hydroxy-5-Nitrobenzeneazo-B-Naphthol. M.W. 309

p-Nitro-o-aminophenol was diazotised as follows:- Add the nitro-aminophenol to water and warm to 40°C. Add sufficient 10 N hydrochloric acid to make solution acid to congo paper and stir well, filtering from insoluble matter if necessary. Cool to 15° C., add remainder of 10 N acid and diazotise at this temperature by adding at once two thirds of the sodium nitrite required (as a 2 N solution). When the reaction to starch-iodide paper has disappeared, the rest of the 2 N nitrite is added as fast as it can be taken up. Allow 15 minutes after the last addition before filtering off the diazo compound.

Repaste the diazo compound with water and ice, and couple with B-naphthol in alkaline solution.

p-Nitro-o-aminophenol	3.85 grams ($^{M}/40$)
Water	75 mls.
Hydrochloric acid (10 N)	6.5 mls.
Sodium Nitrite (2 N)	13.0 mls.
B-Naphthol	3.55 grams.

The dyestuff separates without the necessity for/

/salting out.

Copper Derivative.

An alcoholic solution of the dye was boiled under a reflux for 10 hours with an alcoholic solution of copper acetate. A red-brown precipitate was formed gradually. The product was freed from any of the original reagents, which might still be contaminating it, by successive treatments with water and alcohol.

% Copper. Found:-17.2; 17.3. Calculated:- 17.3% The product contains 1 atom of copper per molecule.

This derivative is slightly soluble in alcohol but insoluble in benzene or water. It is resistent to the action of alkalies and dilute acetic acid.

Chromium Derivative.

This was prepared by refluxing the dyestuff with chromium acetate in alcoholic solution for 5 hours. On addition of water to this solution the complex is thrown down as a very colloidal precipitate. The product has to be washed very thoroughly with acetic acid to remove chromium acetate adhering to the precipitate.

% Chromium. Found:- 10.1; 9.9. Calculated:- 10.2. This compound has 2/3 atom of chromium per molecule.

It is soluble in alcohol giving a red-violet solution/

/solution, but insoluble in water and benzene; stable to alkalies but attacked by dilute mineral acids.

<u>o-Aminophenol-p-Sulphonic Acid→B-Naphthol</u>(Chrome Fast Violet B)

Colour Index 169. M.W 366.

<u>Copper Compound</u> was prepared by boiling an aqueous solution of the purified (by boiling in water) commercial dye with copper sulphate. It is obtained as a red-brown powder which is sparingly soluble in water, alcohol and benzene. The dyestuff was also prepared from its intermediates and treated as above.

	1st Preparation.	2nd Preparation
% Copper :-	20.5; 20.55	19.8; 19.75
% Sulphur :-	7.84; 7.7	7.8; 7. 5
$\therefore \frac{\text{Copper}}{\text{Sulphur}} =$	$\frac{1.33}{1}$	$\frac{1.31}{1}$
$\therefore \frac{\text{Copper}}{\text{Dyestuff}} =$	$\frac{1.33}{1}$	$\frac{1.3.}{1}$

<u>Chromium Compound</u>. This was prepared by boiling the dyestuff with chromium acetate for 5 hours. To isolate the complex the solution has to be evaporated and saturated with salt. 30% excess of the metallising agent was used. The extreme solubility of this product causes it to be obtained largely mixed with salt.

% Chromium :- 5.4; 5.4.
% Sulphur :- 2.9; 2.9.

$$\therefore \frac{\text{Chromium}}{\text{Sulphur}} = \frac{1.1}{1} \text{ atoms} \qquad \therefore \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{1.\ \text{atom}}{1\ \text{molecule}}$$

It is partly soluble in alcohol and insoluble in benzene. No free chromium could be detected in the complex, showing that the metal had not entered the sulphonic acid group.

2-Hydroxy-5-Nitrobenzeneazo-B-Naphthol-6-Sulphonic Acid.

M.W. 391.

This dyestuff was prepared by diazotising p-nitro-o-aminophenol, (see page 100) and coupling with Schaffer's Salt. It is a dark green powder

Copper Complex. This can be prepared simply by adding copper acetate to a solution of the dyestuff, with constant stirring. It is a brown powder slightly soluble in water. Part of its copper content is removed by alkali, but the remainder, being within a complex, is resistant.

% Copper :-	18.7;	18.7
% Sulphur:-	6.48;	6.43

$$\frac{\text{Copper}}{\text{Sulphur}} = \frac{1.47}{1}\text{ atoms} \quad \therefore \frac{\text{Copper}}{\text{Dyestuff}} = \frac{1.47\text{ atoms}}{1\text{ molecule}}$$

This compound has therefore 1½ atoms of copper per molecule.

Chromium Complex. 5 grams of the dye were refluxed for 5 hours with 4.4 grams of chromium formate. The solution was evaporated from about 200 mls. to 50 mls. and the complex salted out.

% Chromium :-	12.9 ;	12.6
% Sulphur :-	5.9 ;	5. 9

$$\therefore \frac{\text{Chromium}}{\text{Sulphur}} = \frac{1.33}{1}\text{ atoms} \quad \therefore \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{1,1/3\text{ atoms}}{1\text{ molecule.}}$$

This derivative was used in the investigation of primary and secondary complexes (see page 54). To convert it into the secondary compound, 5 grams of the chromium complex were heated at 105 - 115° C for 7 hours, in a sealed tube, with 50 mls. of water and 1 ml. of conc. hydrochloric acid. (According to B.P.446,820). On evaporating this solution and filtering, the secondary compound was obtained.

% Chromium. Found 12.0; 11.7 Calculated 11.9

This secondary compound contains 1 atom of chromium per molecule.

The secondary compound gives a red-violet aqueous solution which does not change on the addition of dilute acid, aq. ammonia or sodium carbonate solution. The primary compound gives a deep blue precipitate with acid and with alkalies there is a slow change of colour from red to blue. The primary compound is the more soluble and gives a precipitate of the free colour acid when acidified. This gives a deep red aqueous solution which changes to blue on addition of aq. ammonia.

2-Hydroxy-5-Nitrobenzeneazo-1-Naphthol-5-Sulphonic Acid. M.W. 391.

The dyestuff was prepared by coupling in alkaline solution, diazotised p-nitro-o-aminophenol (see page 100) and 1:5-naphthol sulphonic acid.

Copper Complex. Dyestuff dissolved in water to give a purplish-red solution; acetic acid added till the blue tinge disappeared; heated to boiling and copper acetate solution added slowly with stirring. A precipitate slowly develops.

% Copper :- 15.2; 15.1.

% Sulphur:- 7.74; 7.8

$\therefore \frac{\text{Copper}}{\text{Sulphur}} = \frac{.98}{1}$ atoms $\qquad \therefore \frac{\text{Copper}}{\text{Dyestuff}} = \frac{\text{1 atom}}{\text{1 molecule}}$.

This derivative gives no precipitate with alkali, but after reduction with "hydrosulphite" a precipitate of copper sulphide is obtained.

Chromium Complex.

This was prepared by boiling 7.5 grams of the dyestuff with 6.6 grams of chromium formate in aqueous solution containing 3 mls. 20% formic acid. On salting out there was obtained as a very colloidal precipitate, the chromium complex.

% Sulphur :- 6.7; 6.9.
% Chromium :- 7.4; 7.3.

$\therefore \frac{\text{Chromium}}{\text{Sulphur}} = \frac{.66}{1} \qquad \therefore \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{\text{2/3 Atom}}{\text{1 molecule}}$.

It gives a violet-red solution in water which shows no free chromium ions until after reduction with "hydrosulphite". It is however sensitive to mineral acids, the free colour acid containing no metal in a complex state.

<u>1-Amino-2-Naphthol-4-Sulphonic Acid→1-Naphthol</u>. Colour Index 201
M.W. = 394.

A. <u>Chrome Fast Cyanine</u>.

<u>Copper derivative</u> of this dyestuff was prepared by boiling an aqueous solution of the dye with copper sulphate, the derivative settling out as a brown powder.

% Copper :- 7.35; 7.4

% Sulphur :- 4.0 ; 3.9

$\therefore \dfrac{\text{Copper}}{\text{Sulphur}} = \dfrac{.94}{1}$ atoms $\qquad \therefore \dfrac{\text{Copper}}{\text{Dyestuff}} = \dfrac{\text{1 atom}}{\text{1 molecule}}$

This compound gives a violet solution in water and in alcohol but is insoluble in benzene. It is resistant to the action of alkalies and dilute acid.

<u>Chromium Derivative</u>. The commercial dyestuff was purified by dissolving in water and filtering from insoluble matter. The dyestuff was salted out of solution three times. The complex was prepared by refluxing an aqueous solution of the azo compound with chromium acetate and salting out the/

/the product. It is a dark blue powder, soluble in water and to a slight extent in alcohol and ether but insoluble in benzene. Resistant to the action of alkalies and dilute acid.

% Chromium :- 3.5 ; 3.5

% Sulphur :- 4.3 ; 4.3

$\frac{\text{Chromium}}{\text{Sulphur}} = \frac{.50 \text{ atoms}}{1} \quad \therefore \quad \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{\frac{1}{2} \text{ atom}}{1 \text{ molecule}}$

B. Eriochrome Blue Black B.

Chromium Compound. This was prepared by refluxing, for about 10 hours, 4 grams of the dyestuff and 2 grams of chromium acetate. The product was purified by repeated salting out.

% Chromium :- 5.85 ; 5.84

% Sulphur :- 5.0 ; 5.0

$\therefore \quad \frac{\text{Chromium}}{\text{Sulphur}} = \frac{.72 \text{ atom}}{1} \quad \therefore \quad \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{2/3 \text{ atom}}{1 \text{ molecule}}$

C. Neolan Blue G.

Before analysis, this commercially prepared chromium complex was dissolved in water, filtered, acidified with acetic acid and salted out. It was found to be contaminated with sodium sulphate and therefore barium chloride was added/

/added to remove the sulphate and followed by sodium carbonate to remove excess barium. When evaporated and salted out, a product was obtained which on analyses gave the following results :-

% Chromium :- 6.5 ; 6.5
% Sulphur :- 3.0 ; 2.9

$$\therefore \frac{\text{Chromium}}{\text{Sulphur}} = \frac{1.33}{1} \text{ atoms} \qquad \therefore \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{1,1/3 \text{ atoms}}{1 \text{ molecule}}$$

Neolan Blue G, unlike the other two chromium derivatives described above, gave a precipitate of chromium hydroxide when boiled with aqueous ammonia.

o-Alkyloxy-o-Hydroxyazo Compounds.

o-Anisidine → B-Naphthol. Colour Index 113. M.W = 278.

This dyestuff was prepared by diazotising o-anisidine and coupling in alkaline solution with B-naphthol. It was purified by boiling with glacial acetic acid, filtering and adding water to precipitate the colour. (This method of purification is recommended by the Colour Index). It must then be treated with water to remove any adhering acetic acid.

Copper Compound.

When alcoholic solutions of the azo compound and copper acetate are refluxed together, combination takes place and the copper derivative of the dyestuff is precipitated, as a finely divided red-brown powder, by addition of water. It is soluble in alcohol but only sparingly soluble in water. Dilute mineral acids split off the copper and it is also sensitive to dilute alkalies.

% Copper :- 10.4 ; 10. 4

1 atom of copper per 2 molecules of azo compound requires 10.4% copper.

Pressure Treatment. A mixture of 4 grams of the azo compound in 200 ml. of alcohol and 10 grams of copper acetate in 20 ml. of water, was heated at 130°C in an oil bath; the mixture being under pressure in a stoppered bottle. Heating was continued for 4 hours and then the product was filtered. The precipitate was boiled thoroughly with water to remove any copper acetate and there remained a green compound (with metallic lustre) which was insoluble in water and sparingly so in alcohol and benzene giving a red solution. It was stable to alkalies, dilute mineral acid and 40% acetic acid.

% Copper :- 19.1 ; 19.2.

1 atom of copper per molecule of azo compound requires 19.5% copper. The low results are probably due to the fact that this compound dissociates when heated and some of the metal is likely to be carried away during sublimation.

When water was added to the filtrate from the pressure treatment, a finely divided red-brown precipitate was obtained. There was insufficient of it for analyses, but qualitative tests indicated that it was identical with the compound obtained by refluxing the azo body with copper acetate as already described.

Chromium Compound.

When an alcohol solution of the azo compound was refluxed with chromium formate, no combination took place.

Pressure Treatment. 3 grams o-anisidine→B-naphthol; 70 ml. alcohol; 3 grams of chromium formate in 25 ml. of water, were heated in a beaker inside an autoclave for 8 hours at 130° C. A dark blue precipitate was obtained when the alcoholic solution was diluted with water. This product, which is insoluble in water but soluble in alcohol, is decomposed by ammonia with complete precipitation of its chromium content.

% Chromium :- 11.4 ; 11.5.

2/3 atom of chromium per molecule of azo compound requires 11.5% chromium. To dry this compound completely it has to be heated in the neighbourhood of 150° C., which indicates that there is some association between it and the solvent.

o-Carboxyl-o-Hydroxyazo Compounds.

Anthranilic Acid→B-Naphthol. Colour Index 214. M.W = 292

This dyestuff was prepared by diazotising anthranilic acid and coupling with B-naphthol in alkaline solution. It is obtained as orange-red crystals which were purified by boiling with glacial acetic acid.

Copper Compound.

3 grams of the azo compound were refluxed for 4 hours in 500 ml. of alcohol with 3.2 grams copper acetate in 50% aqueous alcohol. The copper derivative separated out as a red-brown powder. It was purified from any copper acetate by boiling with very dilute acetic acid. It is sparingly soluble in water, giving an orange yellow solution. Dilute mineral acids and alkalies remove the metal from its combination with this azo compound, as also do the usual reagents for copper such as hydrogen sulphide and potassium ferrocyanide. It is dissociated by heat.

% Copper :- 17.6 ; 17.7

1 atom of copper per molecule of azo compound required 18.1% of copper

This derivative was also prepared from cuprammonium sulphate as follows : - 4 grams of the azo/

/azo compound in 500 ml. of water were refluxed with cuprammonium sulphate. (Containing 6 grams copper sulphate and 20 ml. of .880 ammonium hydroxide). The brown copper derivative was precipitated immediately but the refluxing was continued for two hours to encourage completion of the reaction. But even after repeated Soxhlet extractions, both with alcohol and water, the product was still contaminated with the original azo compound and with copper acetate. This method of preparation was therefore judged unsuitable for the purpose.

Chromium Compound.

3 grams of the dyestuff; 6 grams chromium formate; 500 ml. alcohol; refluxed together for 4 hours. When this solution is diluted with water the chromium derivative is thrown down as a red powder. It was purified by boiling with 40% acetic acid.

% Chromium :- 13.0 ; 12.9

% Nitrogen :- 6.70. 6.87

$$\frac{\text{Chromium}}{\text{Nitrogen}} = \frac{1.03\text{ atoms}}{2\text{ atoms}} \quad \therefore \quad \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{1.\text{ atom}}{1\text{ molecule}}$$

This compound is abnormally resistant to acetic acid as was shown by the following experiment. A solution in glacial acetic acid of the dyestuff and chromium/

/chromium acetate was boiled. Combination took place and the chromium complex could be precipitated by addition of water. Heating was however continued almost to dryness, at which stage excess of the original azo compound was decomposed into B-naphthol and a tarry residue while the chromium complex was still intact.

Solochrome Red B. Colour Index 216. M.W. = 452.

Anthranilic Acid→2-naphthol-3:6-disulphonic acid.

For these experiments the commercially prepared dyestuff was used, after dissolving in water and filtering to remove any foreign matter.

Copper Compound.

A mixture of 10 grams dyestuff; 16 grams copper acetate; 400 ml. water, was refluxed for 6 hours. A brown-red copper derivative is deposited on cooling. It is slightly soluble in alcohol, insoluble in benzene and gives a brown-red solution with water. Boiling alkali gives no precipitate of copper oxide with this solution, but hydrogen sulphide gives the usual precipitate. A bulky precipitate of copper "sulphide" is obtained, after reduction with/

/with "hydrosulphite" in alkaline solution.

% Copper :- 22.2 ; 22.2

% Nitrogen :- 4.91; 5.03

$$\frac{\text{Copper}}{\text{Nitrogen}} = \frac{1.96}{2} \text{ atoms} \qquad \frac{\text{Copper}}{\text{Dyestuff}} = \frac{\text{2 atoms}}{\text{1 molecule}}$$

Chromium Compound.

10 grams of the dyestuff; 15 grams chromium acetate and 400 ml. of water refluxed for 6 hours. No precipitate was obtained, even after saturating the solution with common salt, but the distinct acidity of the mixture indicated that the reaction had taken place. The solution was evaporated down and sulphuric acid added to precipitate the free colour acid. This is a red powder which, after reduction with "hydrosulphite" gives a precipitate of chromium hydroxide. Ammonium hydroxide does not precipitate chromium hydroxide from the aqueous solution. This complex is stable to boiling alkalies and dilute mineral acid. The product was very largely contaminated with common salt, which accounts for the small percentages of metal and nitrogen :-

% Chromium :- 2.30 ; 2.35.

% Nitrogen :- 1.20 ; 1.30

$$\frac{\text{Chromium}}{\text{Nitrogen}} = \frac{1.03}{2} \text{ atoms} \qquad \therefore \quad \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{1}{1}$$

o-Amino-Azo Compounds.

o:o'-Diaminotoluene-p-sulphonic acid→m-phylenediamine.

Colour Index 333. M.W. 355.

Toluylene Brown G.

Copper Derivative. 10 grams of the purified commercial dyestuff were refluxed with 10 grams copper acetate in 500 ml. of water for six hours. Then evaporated to about 250 ml. and filtered. The brown precipitate was sparingly soluble in water, slightly soluble in alcohol and insoluble in benzene. When boiled with alkali there was a slight precipitate of copper hydroxide but after filtering this off and reducing the filtrate with "hydrosulphite" a more bulky precipitate of copper sulphide was obtained, thus showing the presence of copper both in an ionised state - in the sulphonic acid group - and in a complex form. The metal is removed from its combination in the complex by dilute mineral acids and even by boiling dilute acetic acid.

% Copper :- 15.6 ; 15.7

% Nitrogen:- 13.8 ; 14.0

$$\therefore \frac{\text{Copper}}{\text{Nitrogen}} = \frac{1.49}{6}\text{ atoms} \quad \therefore \frac{\text{Copper}}{\text{Dyestuff}} = \frac{1\frac{1}{2}\text{ atoms}}{1\text{ molecule.}}$$

Chromium Derivative.

10 grams of the purified commercial dyestuff were refluxed with 20 grams chromium acetate in 800 ml. of water for six hours. The solution was then filtered and the brown precipitate purified from any chromium acetate that might be in it by boiling with dilute acetic acid. This would also remove any chromium that was combined with the sulphonic acid group, but was necessary in order to ensure that the finely divided - almost colloidal - precipitate was not contaminated with some of the excess chromium acetate. The derivative is sparingly soluble in water and alcohol but gives a brown-red solution with sodium hydroxide which deposits chromium hydroxide when reduced with "hydrosulphite". It is sensitive to dilute mineral acid, the metal being removed from the complex.

% Chromium :- 5.64 ; 5.55

% Nitrogen :- 14.5 ; 14. 6

$$\therefore \frac{\text{Chromium}}{\text{Nitrogen}} = \frac{0.62}{6} \text{ atoms} \qquad \therefore \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{2/3 \text{ atom}}{1 \text{ molecule.}}$$

Metallic Derivatives of o-Aminophenols.

o-Aminophenol.

Copper Compound.

13 grams o-aminophenol refluxed with 17 grams copper acetate in about 500 ml. of water for one hour. A grey - black powder, insoluble in water, was obtained. It is slightly soluble in alcohol, giving a brown solution from which copper hydroxide is precipitated by the addition of alkali. It is insoluble in benzene. The metal is removed from its combination by dilute mineral acids. This instability of the metal linkage was responsible for the failure to diazotise and couple this derivative.

4:2:1-Nitroaminophenol.

Copper Compound.

13 grams 4:2:1-nitroaminophenol refluxed for 1 hour with 23 grams copper acetate and 400 ml. of water. A bright green precipitate was obtained which was insoluble in water but decomposed by mineral acids giving a copper salt and a salt of the original aminophenol. When the filtrate, from the above preparation, was treated with salt/

/salt, there was precipitated a small amount of a yellow compound. There were indications that here the metal was held in complex union, for when boiled with alkali no precipitate was obtained, yet when a portion of it was ashed a residue of copper oxide remained in the crucible. However there was insufficient of it for analyses.

Chromium Compound.

15.4 grams 4:2:1-nitroaminophenol refluxed with 11 grams chromium fluoride, 13.6 grams sodium acetate and 500 ml. of water (cf.B.P. 15456/15). A bulky red-brown precipitate was obtained which contained the metal in combination with the aminophenol but was broken down by acids and alkalies, indicating that only the phenolic group was implicated, and there had been no complex formation.

From the filtrate, however, there was salted out a small quantity of a yellow compound. This gave a residue of chromium oxide when ashed. Its aqueous solution gave no sign of chromium with aqueous ammonia, but after boiling with "hydrosulphite", chromium could be/

/be detected. There was not enough of it for analyses, since the insoluble derivative is obtained in almost a quantitative yield.

% Chromium in insoluble derivative :-

Found 9.95 ; 9.95 . Calculated 10.0

1/3 atom of chromium per molecule.

The same results as above were obtained when chromium formate was used in the preparation instead of chromium fluoride and sodium acetate.

o-Amino-o-Hydroxyazo Compounds.

4:2:1-Nitroaminophenol→1:3-phenylenediamine-4-sulphonic acid.

Chrome Brown T.V. Colour Index 98. M.W. 375.

Copper Compound. 10 grams of the purified commercial dyestuff were refluxed with 10 grams cuprammonium sulphate in 300 ml. of 50% aqueous alcohol for one hour. Filtered off the dark brown powder, which was slightly soluble in water, giving a dark brown opalescent solution, and insoluble in alcohol or benzene. To purify it from cuprammonium sulphate, it was washed repeatedly with ammonia.

When alkali is added to the aqueous solution, it gives a precipitate of copper hydroxide. After filtering and boiling the filtrate with "hydrosulphite", a further precipitate - of copper sulphide - is obtained. When boiled with mineral acid, the colour acid is thrown down. This gives a clear red solution with alkali and on reduction with "hydrosulphite" the complex is broken down and copper precipitated.

% Copper :- 20.0 ; 20.1

% Sulphate:- 6.93; 7.05

$\therefore \frac{\text{Copper}}{\text{Sulphur}} = \frac{1.45}{1}$ atoms $\quad \therefore \frac{\text{Copper}}{\text{Dyestuff}} = \frac{1\frac{1}{2} \text{ atoms}}{1 \text{ molecule}}$

Chromium Compound.

10 grams of purified Chrome Brown T.V. refluxed with 8 grams chromium formate in 250 ml. of water for one hour. The red-brown product was filtered off. It is slightly soluble in water giving a brown solution from which some of the chromium is precipitated by alkali but the remainder, only after reduction; showing the existence of chromium in both an ionised and a complex form. The free colour acid is formed, but not precipitated since it is more soluble, by the addition of mineral acids. The chromium which is in complex form is not split off by dilute mineral acid.

% Chromium :- 11.3 ; 11.4

% Sulphur :- 6.57 ; 6.60

$$\therefore \frac{\text{Chromium}}{\text{Sulphur}} = \frac{1.05}{1} \text{ atoms} \qquad \therefore \frac{\text{Chromium}}{\text{Dyestuff}} = \frac{1 \text{ atom}}{1 \text{ molecule}}.$$

SUMMARY.

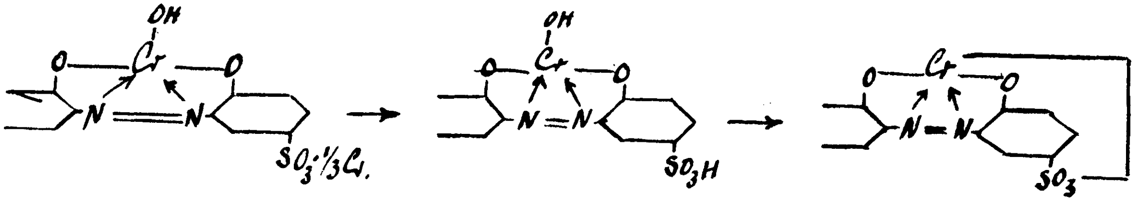
The investigation of the mono-o-hydroxyazo compounds showed that these compounds formed metallic derivatives with comparative ease. This seems to be in accord with the concensus of published work on the subject, though disputed by some of the foremost investigators. An interesting point that arose, was that copper seems unable to form a complex with mono-o-hydroxyazo sulphonic acids, unless the sulphonic acid group has been neutralised. In this respect, this class is inferior in lake forming properties to the di-o-hydroxyazo compounds.

It appears that, in general, with o:o'dihydroxyazo compounds metallisation results in the formation of typical inner complex compounds, both hydroxyl groups acting as acidic groups and either one or both of the azo nitrogen atoms co-ordinating with the metal. However, the experiments have led also to the conclusion that, several different derivatives of the same metal can be prepared from the one dyestuff; the differences being in the proportion of metal combined with the dyestuff and being accounted for by one of the following reasons;

/free sulphonic acid group; metal retaining within the complex some residual basicity; some of the hydroxyl groups may not have combined with the metal through hydrogen replacement, but merely by co-ordination.

The experiments with "primary" and "secondary" complexes leads to the following suggested mechanism for the conversion of one to the other.

Primary complexes contain monobasic chromium. The first reaction in the passage of a primary into a secondary complex is the formation of the free sulphonic acid of the former and this combines with the monobasic chromium already in the complex to give an even more internally bound inner complex salt.



PRIMARY

SECONDARY

The above represents the suggested course of the change.

When taking into account the co-ordinate links between the metal and the azo nitrogen atoms, it is apparent that a compound represented as the secondary one is, would be linked to the dyestuff molecule at five points. Such quinquidentate chelate compounds do not seem to have been recorded in the literature hitherto.

The claims in the patent literature were confirmed - that an o-alkyloxy group can give rise to metallic derivatives, if the conditions of the reaction are such as first to hydrolyse the alkyloxy group. This can be done by metallising under pressure - a method which was found to facilitate complex formation and to encourage the maximum combination between dyestuff and metal.

In the o-carboxyl-o-hydroxyazo compounds, it was found that an o-carboxyl group, though it resembles an o-hydroxyl, results in the formation of a slightly less stable link between the azo compound and the metal.

The experiments with Toluylene Brown G indicated that an amino group o-to the azo link acts similarly to an hydroxyl group, i.e. by hydrogen displacement/

/displacement it can combine with copper or chromium forming part of a chelate group and there were no signs of triazol formation. The reactions of Chrome Brown T.V. (in which there is both an o-amino and an o-hydroxyl group) supported this conclusion.

The test with the Grignard Reagent showed that chromium lakes sometimes contain the metal in a monobasic state.

James L. Boyle
February 1939.