COLOURED AND MODIFIED CEMENTS

A thesis submitted

by

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CONTENTS

COLOURED AND MODIFIED CEMENTS

In recent years, coloured cements have found great favour and there is reason to believe that their use will become more extensive in the future. Coloured cements are usually prepared with white Portland cement as the basis. We are not yet producing a cement of this quality in India. The objection to the use of grey cement as the basis of coloured cements is two-fold; a larger percentage of the colour has to be added and the same degree of brightness cannot be obtained in the ultimate shade. Moreover, grey cements are only suitable for the production of colours such as dark reds, dark browns and other deep tints, and are definitely excluded in the case of lighter shades.

The possibility of the manufacture of white Portland cement (a normal Portland cement containing a low percentage of iron) in India has been discussed earlier (Kudva, M.Sc.Tech. Thesis, University of Bombay, 1939), and a comprehensive summary of the literature on the manufacture of coloured cements has been given also.

For economic reasons in regard to the quantity of pure pigment required for a given shade, the cement colourist must resort in many instances to organic colours. This is especially true when he has to prepare a good blue or green cement. Aesthetic considerations would also often necessitate the use of organic colours. For this reason a thorough study of the fastness properties of organic colours representing all the common types was undertaken with a view to their use as cement colours. The first part of the work constitutes a systematic investigation of a wide range of organic dyes as cement colours. In addition, a very large number of inorganic pigments have also been fully examined.

Fastness tests and standards ~~of~~ for coloured cements:

The tentative measure of fastness properties of coloured cements put forward earlier (loc..cit.) was only iconcerned with light fastness and suffered from other disadvantages. All the samples were exposed to sun-light during the months of March to May, 1938, and the intensity of sun-light naturally varied during the period. The hours of sun-light were measured as hours of bright "sunshine" as recorded at th the Colaba Observatory. This standard of sunshine itself is arbitrary. (2) The humidity varied widely during the period. Actually there was a drizzle of rain on certain days. (3) Exposures were continued until none or very little of the original predominant tint in the exposed sample remained after exposure; a procedure involving the tedious daily measurements of colour units by means of a Lovibond tintometer. In view of these difficulties involved in the former method, a more accurate procedure, which would at the same time be suitable for rapid routine determinations, was obviously necessary. In the present method, the source of light employed was constant; a consistently uniform degree of humidity of the atmosphere was maintained; the fading was observed after exposing only one half of a sample, the other being covered and a sample being considered to have "faded" when the exposed portion showed the faintest, but definite, change of depth or tone from the unexposed part. The end point, therefore, was the development of a line of demarcation between the two halves.

The source of light employed was the Calico Printers' Association ~~Association~~ lamp. The length of the carbon arc was 1 1/2", the humidity about 80%, and the temperature varied between 42°-46°C. Eight grades of fastness were evolved, based on the number of hours of exposure of a coloured cement sample required to produce a distinct alteration in depth or tone, following textile practice (Report of the Committee of the Society of Dyers and Colourists on the work on fixing standards for light, perspiration and washing, 1934; The American Association of Textile Chemists and Colourists Year Book, p. 94; R. V. Bhat, M.Sc.Tech. Thesis, University of Bombay, 1938). In determining the grades of fastness, certain popular commercial dyes and pigments were employed as primary standards for the obvious reason that coloured cements prepared from these required definite convenient intervals to bring about fading. The following are the hours and the corresponding grades of fastness to light:

Grade	Hours
1	5
2	10
3	17
4	23
5	50
6	71
7	96
8	120

The fastness to washing was classified into five grades as in the case of textiles, the maximum being 5. The fastness was considered 5 if the coloured cement did not bleed when treated with boiling water, while 4 represented those coloured cements which though bleeding slightly at the boil did not bleed at room temperature, while 3, 2 and 1 represented respectively those which bled at room temperature slightly but with no alteration in the shade of the cement, those which altered in shade with or without bleeding, and lastly those whose colours were completely removed.

On this standard 3 commercial coloured cements, whose colouring ingredients were respectively an azo colour (yellow), a phthalocyanine (blue) and an iron lake of a nitro naphthol (green), had light fastness grades of 2-3, 8, and 7, and washing fastness grades of 4, 5 and 3. ~~In the table of fastness properties 1 represents the fastness properties as determined by the earlier method. while~~

The fastness properties of coloured cements: The basic dyes were investigated first. The lakes of these dyes were precipitated by tannin, Katanol and complex mordants such as silico-tungstic, phospho-tungstic and phosphomolybdic acids, and a Green Earth of an Indian origin. Although the lakes precipitated by the complex mordants were comparatively faster, they nevertheless left much to be desired as cement colours. A large number of azo dyes, both acid and substantive*, were precipitated as their barium lakes, and these were used as cement colours. The results, however, were not encouraging. Substantive dyes were applied by dissolving the dyes in water used for gauging the cement. These dyes react with the calcium of the cement to give a lake in the body of the cement itself. On ageing, the coloured cement was fast to washing, but the fastness to light was only 1-2. The water-soluble mordant azo dyes containing co-ordinated chromium or copper (Palatine Fast and Neolan colours) were employed for colouring cement in a similar manner to the substantive dyes; the fastness to light was about 4. Casein was dyed with these dyes as in the case of wool, and this was ground up with cement, but the resultant coloured cement did not show an improved fastness to light. A number of commercial organic pigments belonging to the azo class were also investigated as cement colours. The fastness properties

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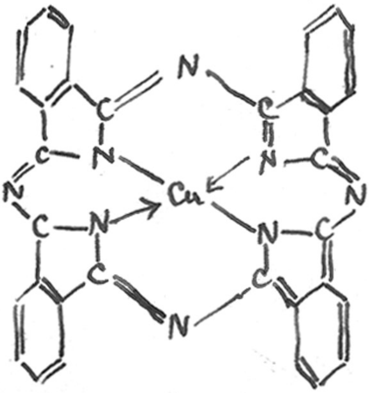
* Footnote: The substantivity refers to cotton.

of dyes obtained from Naphtols and diazonium compounds on cement, applied in the dry state by grinding up with white Portland cement and applied by dyeing the cement as in the case of textile fibres, showed a remarkable difference from their fastness properties on textile fibres. In the former case the fastness to light was 1-2, while in the latter in some cases it was as much as 7. The alkaline nature of cement and the marked substantivity of the Naphtols to cotton were apparantly two directions in which the course of the deterioration in fastness in the case of cement was to be sought. The fastness to washing of cements coloured with the azoic dyes was in general excellent. Since the discovery of Indanthrene Blue by Bohn in 1901, the anthraquinone vat colours have proved to be of outstanding excellence in regard to their fastness properties, so far as the dyeing and printing of textiles are concerned. Their main disadvantage is the cost. Examined from the present point of view, vat dyes of the anthraquinone type lacked covering power when applied in the dry state, but when the cement was dyed by the usual method of reduction and oxidation of the vat colours, a small percentage, of the order of 0.25%, was sufficient to produce full shades.

The fastness to light of vat dyes on cement ranged from 5 to 8. In the case of Indanthrene Blue GCD and Indanthrene Brilliant Green B, the coloured cement (dyed from a vat) actually became slightly darker on prolonged exposure. The alizarines were only moderately fast in their fastness properties. A number of pigments of nitroso derivatives of some Naphtols were synthesised and their fastness properties were determined. These exhibited the highest fastness properties of all the organic pigments, and were in this respect of the same order as the phthalocyanine pigments. Among the inorganic pigments, several of the commercially employed cement colours were examined. These generally had the highest fastness properties, both to light and washing. A number of iron oxide colours were prepared from the reduction sludge of organic nitro compounds. Like the commercial oxide colours, these showed maximum fastness properties.

The results indicate briefly that the anthraquinone vats, the Phthalocyanine pigments and the lakes of nitroso derivatives of the Naphtols synthesised in the present work were the only organic colours which were comparable in fastness properties to inorganic pigments used in technical practice for the manufacture of coloured cements. But in regard to the brightness of shade and covering power, or the weight percentage required to produce a given shade, the organic pigments were greatly superior to the inorganic pigments. For example, 20% of a manganese blue marketed as "Cement Blue failed to produce the same depth of shade as a 0.5% of a blue phthalocyanine pigment.

It would seem from the results that organic lakes would show a high fastness to light (apart from the anthraquinone vat dyes) only when they form co-ordination complexes with metal atoms. For example, the blue phthalocyanine pigment is a copper compound of the structure



and its remarkable fastness properties are ascribed to the structural complexity of the heterocyclic ring involving the copper atom. Likewise it was found that the nitroso derivatives of the Naphtols gave metallic lakes of excellent fastness properties. For this reason a series of lakes of the nitroso derivatives of the Naphtols were prepared. The structure of these complexes could be best explained by the application of the co-ordination theory.

The co-ordination theory: The co-ordination theory of valency was first employed to elucidate the molecular structure of such compounds as the ammoniates of trivalent cobalt, the numerous complex cyanides, and the alums. (cf. Sidgwick, "The Electronic Theory of Valency", 1932 Ed., p. 188; Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry", 1938 Ed., p. 79; Ephraim, "Inorganic Chemistry", 1939 Ed., p. 277; Morgan and Burstall, "Inorganic Chemistry", 1936 Ed., p. 291).

Werner first postulated, without involving any special theory of valency, that neutral molecules or oppositely charged 'ions' are grouped or co-ordinated around a central ion in the "first sphere of attraction", or "the co-ordination sphere". The number of groups which may be so arranged about the central ion is the co-ordination number, and is characteristic of that ion, and in general this number assumes values of 2, 3, 4, 6 and 8, which allows of spatially symmetrical arrangements, the values 6 and 4 being most common.

Taking for instance hexammine cobaltic chloride, six ammonia molecules are co-ordinated about the cobaltic ion forming a new trivalent cobaltic complex ion $(CO(NH_3)_6)^{3+}$; the chlorine is bound in the "second sphere of attraction", i.e. it exists as an independent anion. The co-ordination of negative ions to a central metal atom is exemplified by the ferrocyanide anion $(Fe(CN)_6)^{4-}$, in which 6 anions surround a central ferrous ion, forming thereby a complex anion with a net charge of 4 units.

As Werner first started with the study of cobaltammines it is as well to examine these compounds first. The following series are a good example:

$$(Co(NH_3)_6)^{+++}, \quad (Co(NH_3)_5\ Cl)^{++},$$

$$(Co(NH_3)_4\ Cl_2)^{+}, \quad (Co(NH_3)_3)Cl_3)^{0}$$

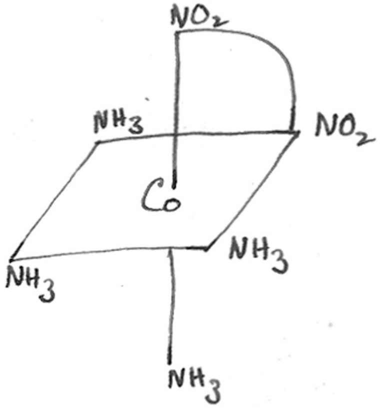
The first complex is a trivalent cation, but substitution by a negative atom or ion (e.g. "Cl") in the co-ordination sphere reduces the valency of the co-ordinated cobalt atom by 1, until finally the valency of the last compound becomes zero, and it ceases to have ionic properties. If the substitution of negative radicals is carried out further the co-ordinated shell will become an anion:

$$(Co(NH_3)_2\ Cl_4)^{-}$$

In other words the co-ordinated inner structure of the cobalt ammine can be a tri-acid base or a tri-basic acid or represent intermediate stages, depending on the net resultant charge on the co-ordinated cobalt shell.

<u>Isomerism in co-ordinated compounds:</u> (1) Werner isolated nine polymeric forms of $(Co(NH_3)_3(NO_2)_3)$. Thus $(Co(NH_3)_3(NO_2)_3)$ was a neutral molecule. In $(Co(NH_3)_4($ In $(Co(NH_3)_4(NO_2)_2)(Co(NH_3)_2(NO_2)_4)$, the first shell had a single nett positive charge and the second a single negative one. Similarly $(Co(NH_3)_5NO_2)(Co(NH_3)_2(NO_2)_4)$ and other forms could be isolated. (2) A simple instance of isomerism arises from compounds like $(Co.Br(NH_3)_5)SO_4$ and $(Co.SO_4(NH_3)_5)Br$. Both, though having the same simple formula, differ widely in their porperties. The first has an ionised sulphate radical, while the latter has an ionised bromide radical. The first gives a precipitate with barium chloride while the latter is precipitated by silver

nitrate, but the first is not precipitated by silver nitrate and the second not by barium chloride. (3) Compounds such as $(Co(NH_3)_6)^{+++}$ $(Cr(CN)_6)^{---}$ and $(Co(CN)_6)^{---}$ $(Cr(NH_3)_6)^{+ \cdot +}$ are not identical, inasmuchas the first has the cobalt shell in the cation, while the latter has it in the anion. (4) The green and violet forms of $\underset{\text{green}}{(Cr.Cl_2(H_2O)_4)^{Cl}(H_2O)_2}$ and $\underset{\text{violet}}{(Cr(H_2O)_6)Cl_3}$ are different compounds, the one having only a single ionised chlorine atom and the other all three in the ionic form. (5) Isomerism can be due to space arrangement also. Assuming for the compound $(Co(NH_3)_4(NO_2)_2)$ an octahedral structure, two isomeric forms become possible.



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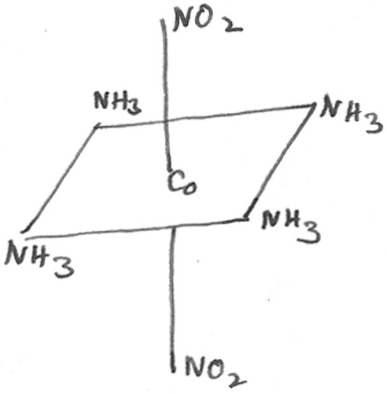
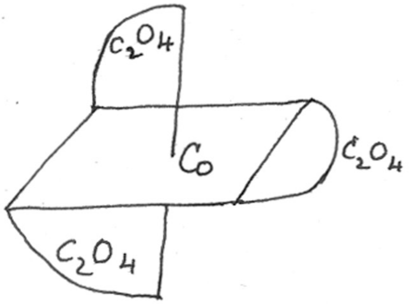
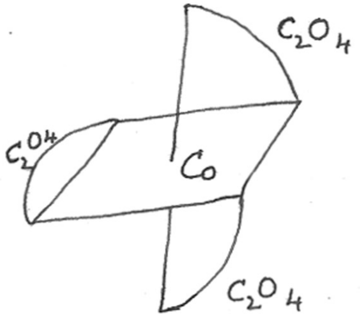


NO_2

The theory of the octahedral arrangement has been fully confirmed by the study of the mirror image forms of compounds by optical means





<u>Electronic interpretation of co-ordination:</u> The units in the first sphere of co-ordination surrounding a central atom are linked to the central atom co-valen~~cy~~tly; this fact was demonstrated by Werner, who showed that they had no ionic properties. The evidence further brought up by geometrical and optical isomerism shows conclusively that Werner's findings are beyond dispute. Thus the maximum co-ordination number of an atom is its maximum co-valency number. In the light of the electronic theory, the cobaltammine series can be viewed differently, e.g. $(Co(NH_3)_3)Cl_3)^{0}$ is the non-ionised cobaltammine compound. If a "Cl" (neutral) atom is removed, it will take with it

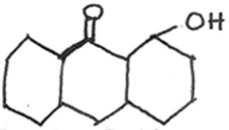
one of the electrons which it previously shared with the central cobalt atom, but will leave the other behind. If now an ammonia molecule takes its place, this provides the two electrons required for its attachment, so that the cobalt has gained one electron by the exchange. Thus the compound has one too many electrons, which it loses and thereby acquires a positive charge. The whole reaction could be graphically represented.

$$(\mathrm{Co}\ \underset{\bullet}{\overset{+}{}}\ \mathrm{Cl})^{0} \qquad (\mathrm{Co}\ ^{+})^{\ 0} \qquad (\underset{+}{\mathrm{C\dot{o}}}\!:\ \mathrm{NH_3})^{0} \qquad (\mathrm{CO}\ :\ \mathrm{NH_3})^{+}$$

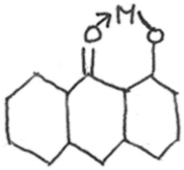
Sidgwick ("The Electronic Theory of Valency", 1927 <u>Ed.</u>, p. 113) has given an example of the change of electro-valency on replacement, which is not characteristic of Warnerian complexes alone. When ammonia acts on methyl chloride, methylamine hydrochloride is formed. The chlorine is replaced by NH_3, and the electro-valency of the complex changes from zero to + 1.

<u>Chelate compounds:</u> It is possible for co-ordination to take place between two atoms which already form part of the same molecule. In that case the product should contain a ring, and these products have been called by Morgan (Morgan and Drew, <u>J. Chem. Soc.</u> 1920, <u>117</u>, 1457)"chelate compounds. Their existence in the mordant dyes was fully

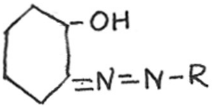
established by Morgan and his pupils. They showed that



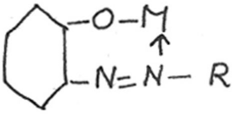
gave with an equivalent of the mordant



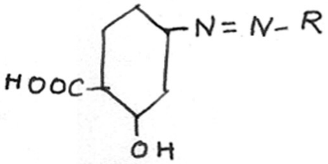
Similarly

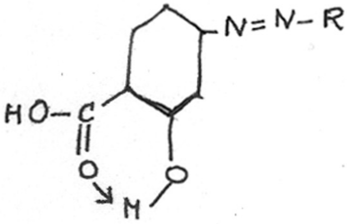


gave



and



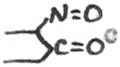


Application of the co-ordination theory to adjective dyeing: The fact that certain dyes, which are called polygenetic, undergo remarkable changes in their shades by employing different mordants in adjective dyeings, and also the characteristic improved all-round fastness properties of these compounds when applied with the aid of a mordant led investigators to foresee the possibility of a stable compound formation between the mordant (metal atom or atoms) and the dye molecule.

Morgan and his colleborators (Morgan and Main-Smith, J. Chem. Soc., 1921, 704; 1922, 160; 1922, 2866; 1924, 1731; Morgan and Moss, J. Chem. Soc., 1922, 2857) in an extensive study of the subject showed conclusively that such dye molecules formed co-ordination complexes in combination with the metal atoms. Incidentally they isolated lakes of various dyes in substance, e.g. (1) hydroxyanthraquinones (2) azo-salicylic acids (3) *o*-dihydroxyazo dyes(4) *o*-carboxy-*o*-hhydroxy azo dyes and (5) quinone oximes. A cobaltammine reagent was emprimarilly employed for lake formation.

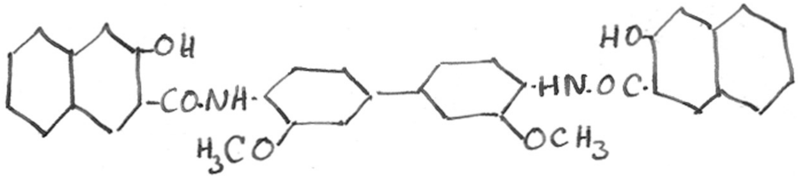
In more recent years Drew and his co-workers have made a valuable contribution to our knowledge of the first four types of compounds by a study of their copper, nickel, chromium, zinc, iron and vanadium lakes (Drew and Landquist, J. Chem. Soc., 1938, 292; Drew and Fairbairn, J. Chem. Soc., 1939, 824; Drew and Beech, J. Chem. Soc., 1940, 603; 608; Drew and Dunton, J. Chem. Soc., 1940, 1064; see also Werner, Ber., 1908, 41, 1062; Baudisch, Z. Zangew. Chemi., 1917, 30, 133; Charrier and Berreta, Gazetta, 1926, 56, 865; Crippa, ibid., 1927, 57, 207; Cremonimi, ibid., 1928, 58, 372; Elkins and Hunter, J. Chem. Soc., 1935, 1598). While Drew's objective would appear to be the elucidation of the mechanism of adjective dyeing and the constitution of complexes formed by the association of metal atoms with mordant dyes, it has been the aim of this investigation in the first instance to investigate the character of the lakes prepared earlier (Kudva, loc. cit.).

The Orthoquinone oximes: In their investigation of the orthoquinone oximes, Morgan and Moss (J. Chem. Soc., 1922, 2857) studied the cobalt and iron lakes of the dioximes of resorcinol. The oximes of the naphthalene derivatives were studied by employing a cobaltammine reagent for lake formation (Morgan and Smith, J. Chem. Soc., 1921, 704). The iron lakes are valuable from the dyer's point of view, and more particularly the calico printer's point of view, and as the pigment in substance the iron lake of nitroso-2-naphthol (Pigment Green B) is being extensively employed in the paint and allied industries.

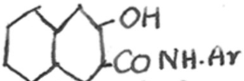
The quinone oximes, while showing characteristic tendency for lake formation with some metals, do not exhibit the same tendency with others. Advantage has been taken of this in analytical chemistry (cf. cobalt and nickel lakes of 1-nitroso-2-naphthol). According to Morgan, the quinone oximes owe their lake formation properties to the presence of at least one unsaturated group  $\left\langle\begin{smallmatrix} N=O \\ C=O \end{smallmatrix}\right.$ capable of taking up two positions in a co-ordination complex surrounding a metal atom, so that the latter becomes finally held in a heterocyclic ring.

Except for Naphtol Green B, the use of nitroso phenols or orthoquinone oximes has been more or less confined to printing, for which, however, they had the disadvantage that the iron lakes were somewhat dull in tone. The nitroso derivatives of Naphtol AS and its analogues appeared to be of special interest in view of the likelihood of lakes of enhanced brightness being obtainable from them. On account of the marked substantivity of the Naphtols, ~~the~~ in comparison with β-naphthol and due probably to the introduction of the carboxylamide (-CO-NH-) group, their nitroso derivatives might have greater interest in dyeing cotton than dinitroso-resorcin and the nitroso naphthols. As in the dyeing and printing, the Naphtols also possess the great advantage that they constitute a series of analogous derivatives of β-naphthol, in all of which the 1-position is free, so that a wide range of nitroso derivatives ~~of~~ and lakes therefrom could be prepared. There is little doubt that some at least of the numerous lakes whose synthesis has thus become possible would prove to be of practical value to the dyer and calico printer, as well as to the cement colourist.

The study of lake formation with quinone oximes has now been extended to the Naphtol AS series. It is conceivable that a symmetrically constituted Naphtol, e.g. AS-BR



could give a dinitroso derivative, a mononitroso derivative; they might or might not give a doubly bound lake, i.e. both the nitroso groups might or might not be involved in the formation of chelate rings. The mono-nitroso compound, if formed, should be capable of giving a lake in which a free coupling position would be available, so that an azo dye could be formed. Further if the diazotised base has an 'OH' or a 'COOH' group in the *o*-position to the amino group, the resulting azo dye would again be capable of co-ordinating with a metal atom. Investigations on these lines are in progress in these laboratories.

While in general the reactions with nitrous acid take place only at low temperatures, it has been found that the reaction does not thus go to completion if Naphtols of the Naphtol AS series  are employed, a temperature of 60°C. or above being necessary towards the end of the reaction.

With dinitroso resorcinol, Morgan obtained a basic ferric lake by employing a ferrous compound

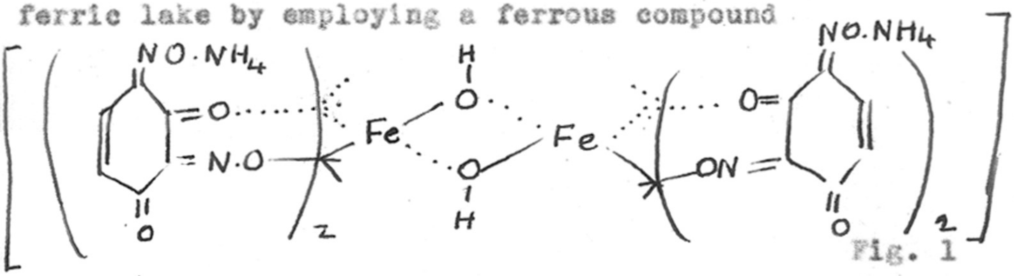


Fig. 1

with a ferric compound be obtained a normal ferric lake

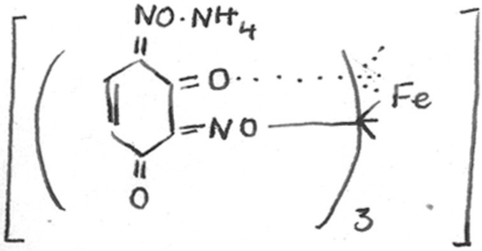
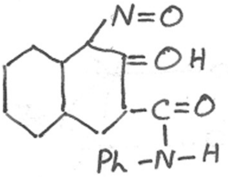
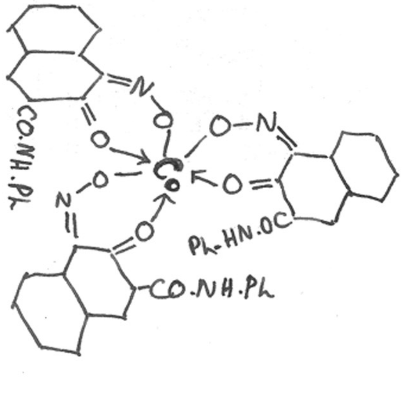


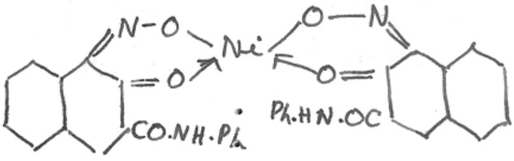
Fig. 2

From the theoretical point of view, nitrosated Naphtol AS and its analogues present interesting possibilities. For example, the compound



can act as a tridentate group like 1:2:3-triaminopropane, and can form a triple attachment to a single metallic atom. With a 6 co-ordinated metal atom two molecules of this compound can occupy the 6 positions in the co-ordination sphere. If, however, the molecule only acted as a bidentate it would require 3 molecules to occupy the 6 positions in the co-ordination sphere of the metal atom. It was found that only a single cobalt atom was associated with 3 molecules of the nitroso compound and a nickel atom with 2 molecules. These compounds were moreover fully saturated co-ordinatively This can only lead to compounds having a graphical structure, such as





With a ferrous salt the lake obtained was a basic ferric lake, the iron being present entirely in the tervalent state

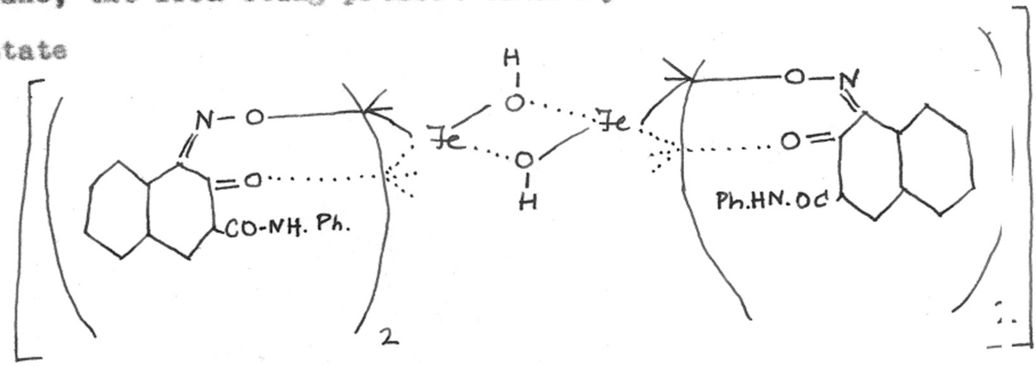
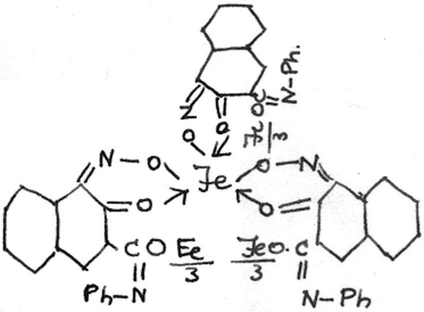
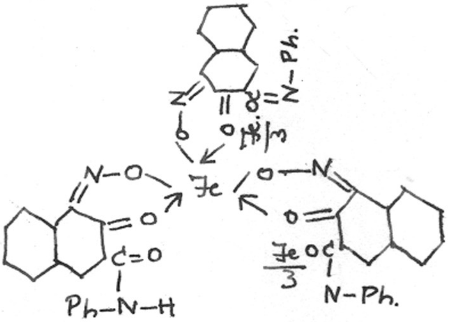
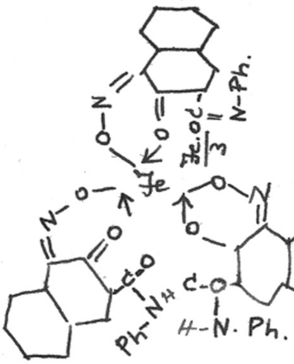


Fig. 5

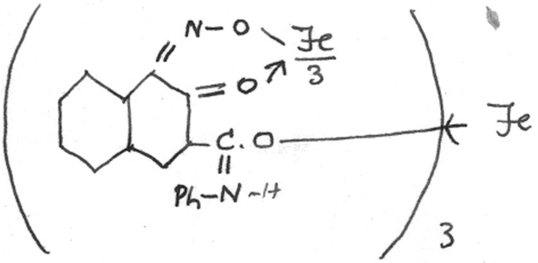
There still exists, however, some confusion in the present case, as well as in the literature, with regard to the valency state of iron (cf. Rowe, "The Development of the Chemistry of Commercial Synthetic Dyes", 1939 <u>Ed</u>., p. 11). A ferric salt gave compounds of three different types:







These variations are due to the possibility of enolisation of the carboxyl group in Naphtol AS (cf. Bhat, Forster and Venkataraman, J. Soc. Dyers Col., 1940, 56, 166). While theoretically we should thus be able to obtain 4 compounds, viz., (1) in which 3 molecules of the nitroso compound hold 1 atom of iron (2) in which the 3 molecules of the nitroso compound, having held 1 atom of iron, one of the 3 molecules will further combine with 1/3 atom of iron due to its enolisation (3) in which 3 molecules of the nitroso compound, having held 1 atom of iron, 2 of the 3 molecules further combine with 2/3 atom of iron due to enol reactivity and finally (4) in which 3 molecules of the nitroso compound having first held 1 atom of iron, further combine 1 more atom, thus



Hence R $\left[(R)_3Fe\right]^{n\frac{Fe}{3}}$

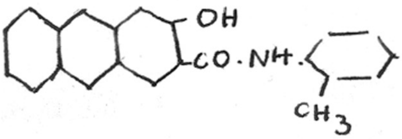
where N = 0, 1, 2, 3 and R is the nitroso residue ~~and n can have the values~~

We have not succeeded in isolating the compound where $n = 0$ or the compound $(R)_3Fe$. Even with an insufficiency of iron the $(R)_3Fe$ compound could not be obtained.

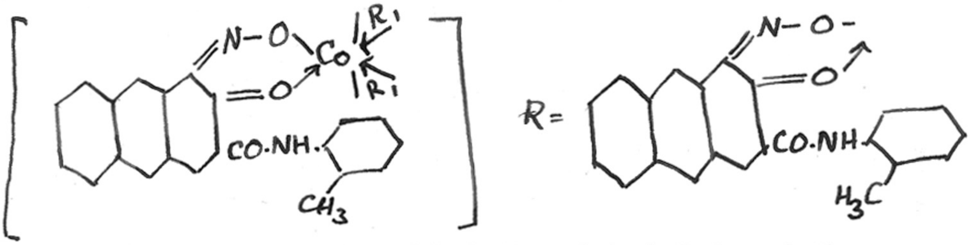
Chromium had the tendency to show the same characteristics as iron in the formation of its lakes. Owing to the solubility of the chromium lake in alcohol, very poor yields of the products were obtained, and these were not of the same degree of purity as the iron compounds. With 1/3 atomic proportion of chromium per molecule of the nitroso compound, the lake obtained invariably contained a higher percentage of chromium than would correspond with the $(R)_3Cr$ type lake. With a large proportion of chromium(1 atom per molecule of nitroso Naphtol) the lake formed was of the $(R)_3Cr_2$ type.

Copper formed a lake similar to the nickel lake.

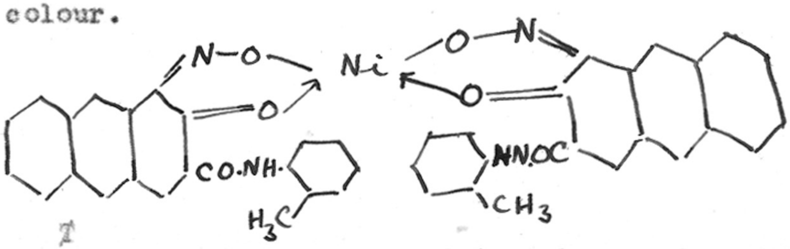
<u>Naphtol AS-GR:</u>



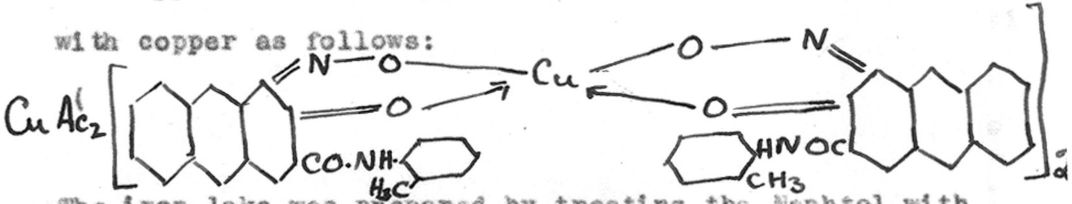
The nitroso derivative was a dull reddish brown and was more insoluble than that of Naphtol AS. The cobalt lake, prepared in a similar manner to the cobalt lake of the nitroso derivative of Naphtol AS, was also characterised by the fact that it had a similar structure to the former:



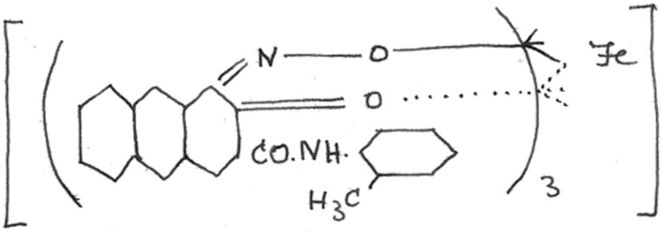
The nickel lake also resembled the nickel lake of the analogous compound from Naphtol AS, but was brighter and redder in colour.



The copper lake was copper red in colour and was associated with copper as follows:

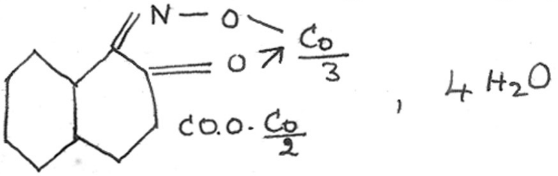


The iron lake was prepared by treating the Naphtol with nitrous acid in presence of ferrous sulphate; the resultant iron lake was a normal ferric lake (R [illegible] which



which conclusively proves the fact that whether we start with a ferrous or ferric salt the lakes of these nitroso derivatives contain iron only in the tervalent state (cf. Morgan and Moss, *loc. cit.*) .

2-Hydroxy-3-naphthoic acid: By isolating the cobaltous cobaltic lake of the nitroso derivative, it has been shown that cobalt can only exhibit its divalency in its simple salts. The lake has been assigned the graphic formula



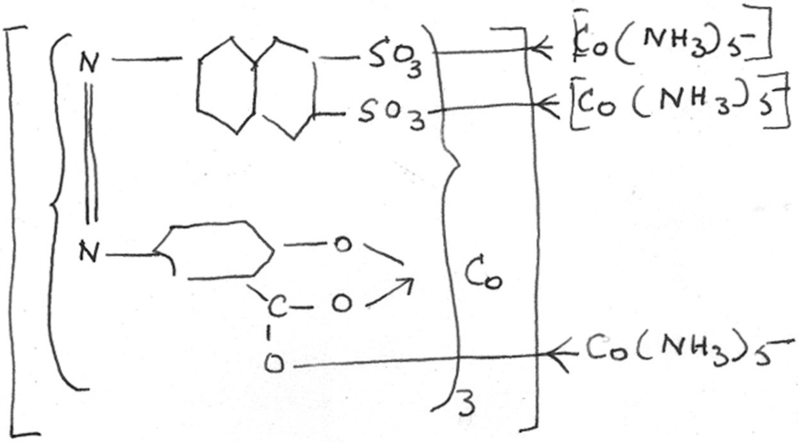
in which the cobalt atom forming a simple salt with the carboxy group is divalent. The di-ferric and the di-cupri lakes have also been isolated.

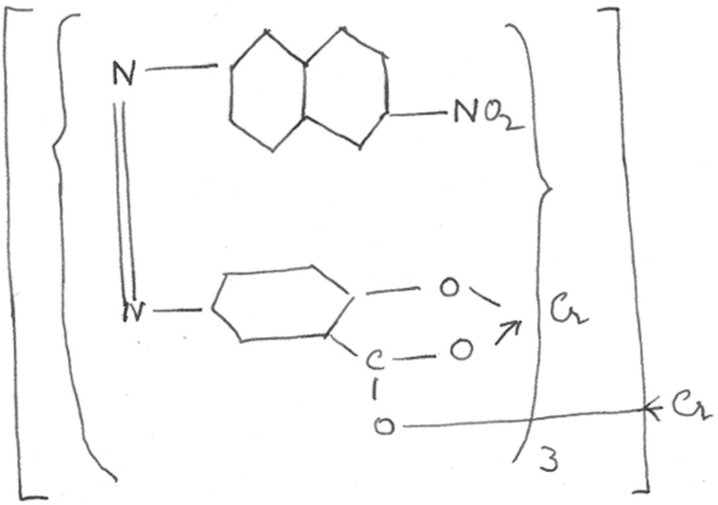
Salicylic acid derivatives: The azo salicylic acids owe their mordanting properties to the "salicyl" residue. The salicyl derivatives of the metals have been extensively investigated. Our interest from the view point of lake formation is centred round the salicyl residue. Courtois

(Bull. soc. chim., 1923, 33, 1761; 1773), Weinland and Hager (Z. anorg. Chem., 1927, 160, 193), Wark (J. Chem. Soc., 1932, 41) and Barbieri (Gazetta (1917), 47 , 252) and Franke (Annalen, 1931, 501, 491) are among the investigators who have prepared complexes of uranium, lead, zinc, nickel, cobalt and iron with salicylic acid. Burrows and Wark (J. Chem. Soc., 1928, 222) in an interesting study of aluminium complexes expected to obtain one or the other of the acids $H(Al(C_7H_4O_3)_2$, $H_3(Al(C_7H_4O_3)_3)$. They were not successful in isolating these compounds, but instead obtained an acid corresponding to the ordinary valency of aluminium and the co-ordination number 4, viz., $H(Al(C_7H_4O_3)_2),2H_2O$; experimental evidence showed, however, that the acid was dibasic, which could be reconciled to the valency of aluminium by regarding the acid as $(H_2(Al(C_7H_4O_3)_2\ OH,\ H_2O)$ in which the co-ordination number of aluminium is 6, the compound being unlike the usual chromic and ferric acids derived from salicylic acid. In fact the alumino acid, though prepared in the absence of water, did contain the aquo and the hydroxyl groups, which fact must be carefully noted. Wark (J. Chem. Soc., 1923, 1816), following on the work of Pickering (J. Chem.

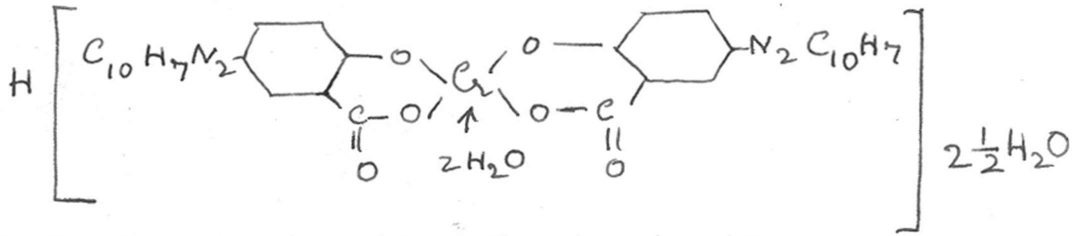
Soc., 1911, 1347) had suggested that the metallic derivatives of the o-hydroxy acids would be stabler, the stronger the acidity of the hydroxyl groups. Hence, while in the aliphatic series the metallic derivatives of lactic and glycollic acids were unstable, the salicylato derivatives were quite stable. In a later investigation, Werk (J. Chem. Soc., 1927, 1753) showed that similar to the sodium salt $Na_2(Cu(C_7H_4O_3)_2)$ of the cupric acid, $H_2(Cu(C_7H_4O_3)_2)$ was the cupric salt of the cupric acid $Cu(Cu(C_7H_4O_3)_2)$. These facts considered along with the results of Morgan (loc. cit.) would naturally present a new aspect of the ch chemistry of the mordant dyes of azo salicylic acid.

Among the lakes prepared by Morgan, the salicylato derivatives were of the following types:

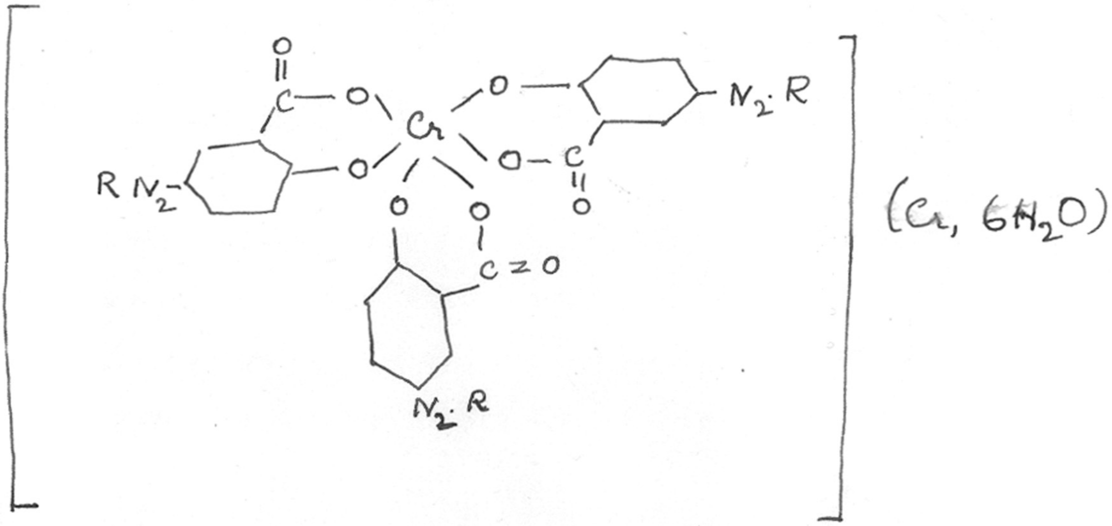


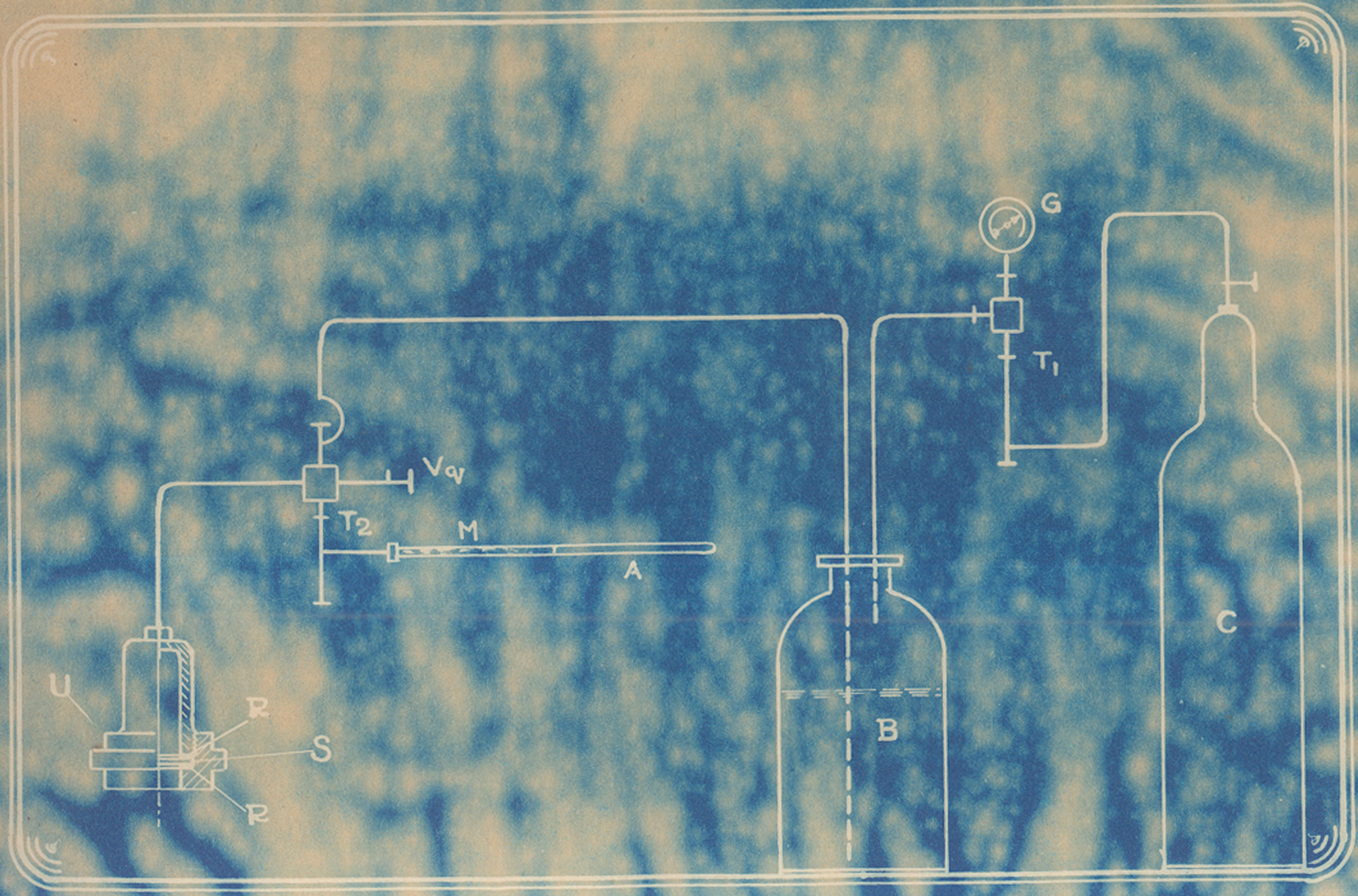


Drew and Fairbairn (J. Chem. Soc., 1939, 823) have isolated the chromic acid

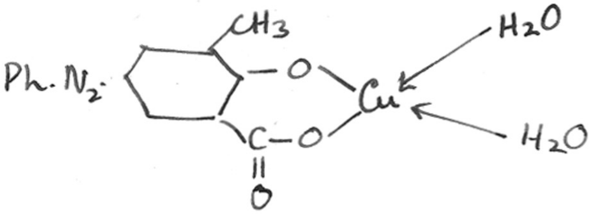


and also the chromi salt of the chromi acid

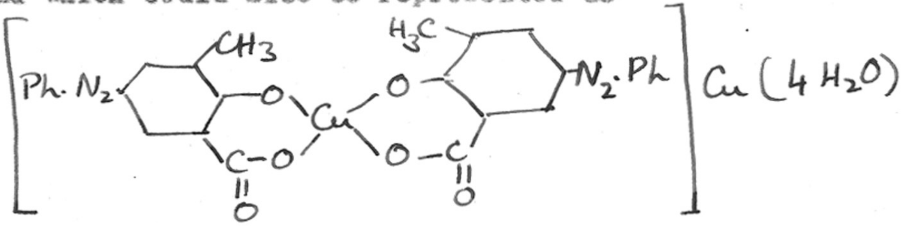



G
T_1
Va
T_2
M
A
C
U
R
S
R
B

which is similar to the lake isolated by Morgan:

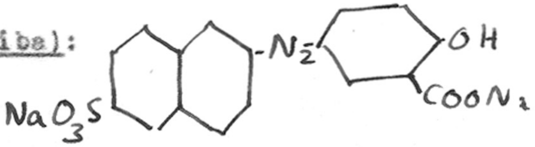


and which could also be represented as

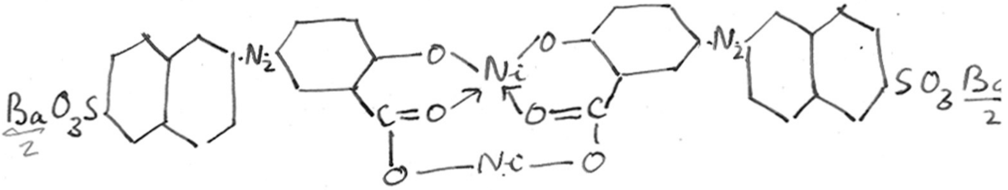


it would then be the analogue of the cupric salt of the cupric acid isolated by Wark.

Chrome Fast Yellow 5G(Ciba):



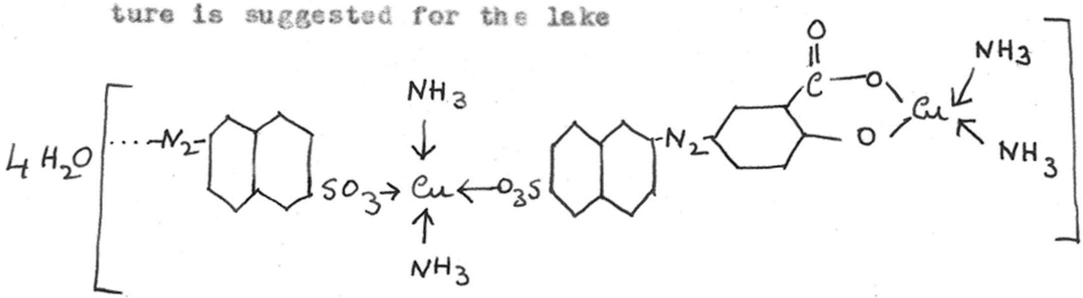
Chrome Fast Yellow 5G (Ciba) gave a simple salt from its aqueous solution on treatment with nickel nitrate, chloride or sulphate. The nickel in this dye salt was ionised and could be precipitated by the characteristic analytical reagent, dimethylglyoxime. The salt was very sensitive to the action of mineral acids, which removed the nickel and gave the dye acid. In the simple nickel salt the nickel was entirely replaceable by barium, which is contrary to what should be expected, if the nickel was involved in an inner complex salt. The fact that nickel is replaceable by barium was not observed originally, and a graphic structure similar to



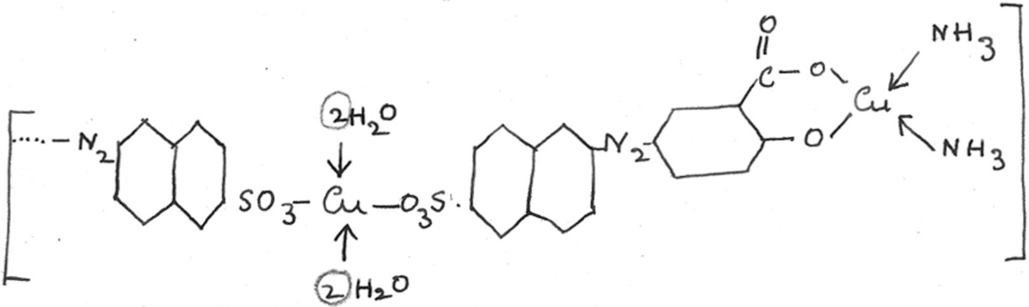
was tentatively suggested, earlier (Kudva, <u>loc. cit.</u>).

The dye gave a simple salt on treatment with cobalt sulphate. The cobalt salt of the dye was exactly similar to the nickel salt, and also yielded a barium salt by the action of barium chloride on its aqueous solution. The cobalt was divalent (cf. Morgan and Smith, <u>J. Chem. Soc.</u>, 1922, 160).

With copper sulphate and zinc chloride the dye gave simple salts. With a co-ordinating amine such as cuprammonium sulphate and aquopentammine cobaltic chloride the respective inner complexes were obtained. The copper lake had the formula ($\frac{3Cu}{2}(C_{17}H_9N_2O_6S)2H_2O.3NH_3$) and out of the 3 molecules of ammonia one was lost on drying, along with 2 molecules of water. But the 2 molecules of water, however, returned on keeping in air. The following graphical structure is suggested for the lake

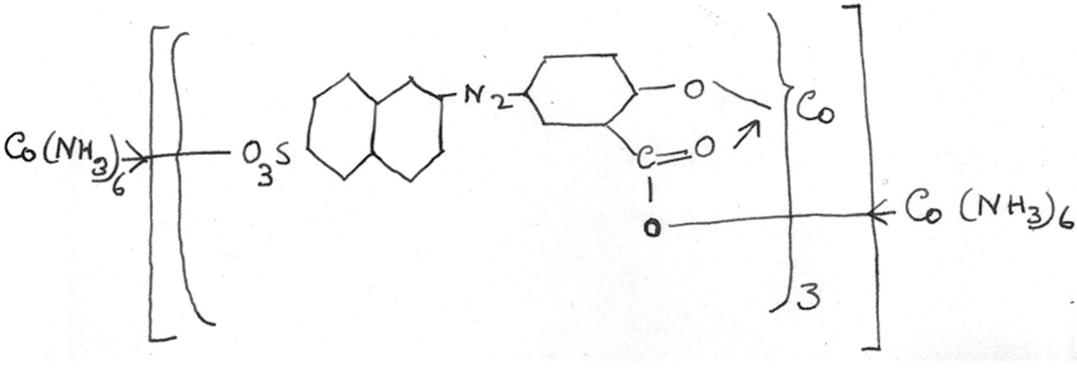


which on desiccating would ~~become~~ change into



after losing 1 molecule of ammonia and 2 molecules of water and regaining 2 molecules of water.

The cobalt lake was of the same form as those obtained by Morgan



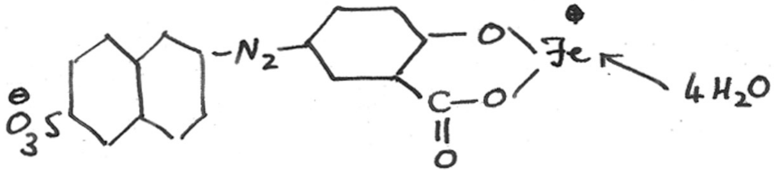
3 molecules of the lake contained 12 molecules of ammonia and 3 atoms of cobalt, and assuming a chelate group in the dye, it was in accordance with Morgan's equation

$6(n - 1) = m$, where n = the atoms of cobalt

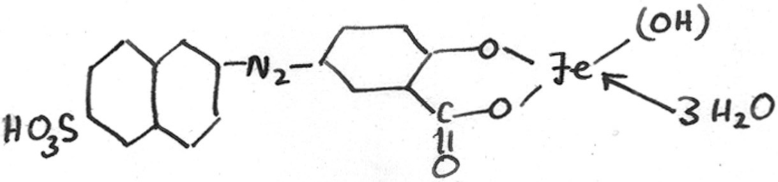
m = the molecules of ammonia,

the cobalt being trivalent.

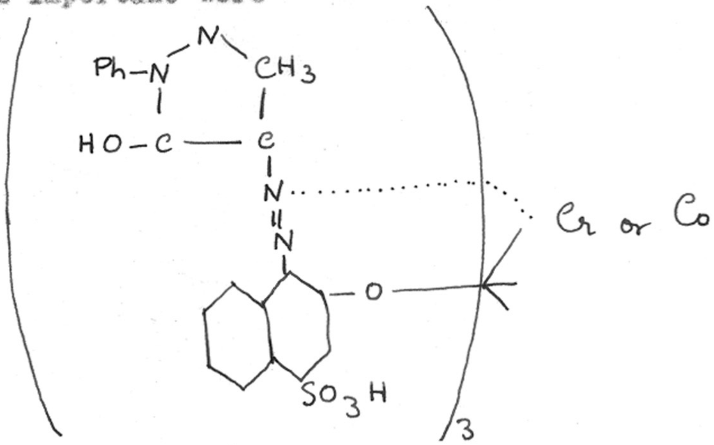
The dye gave with vferric chloride a lake with 4 molecules of water. On desiccating 3 molecules of water were lost, the lake apparently undergoing a modification



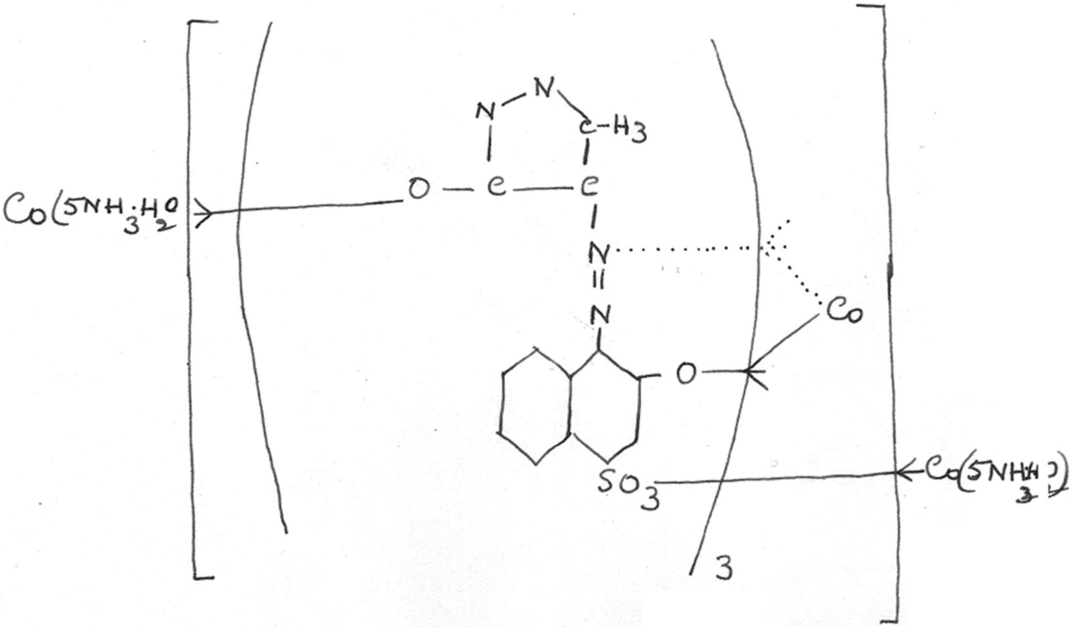
The lake regained the 3 molecules of water when kept in air, giving probably

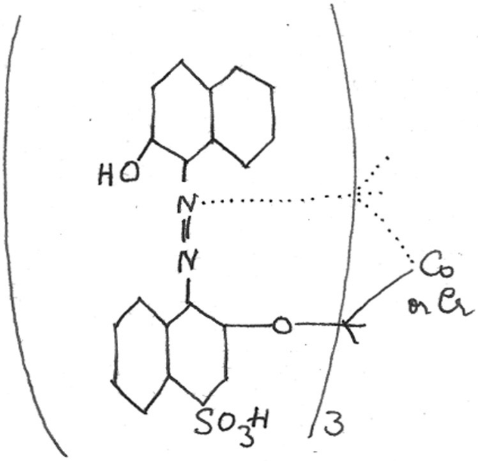


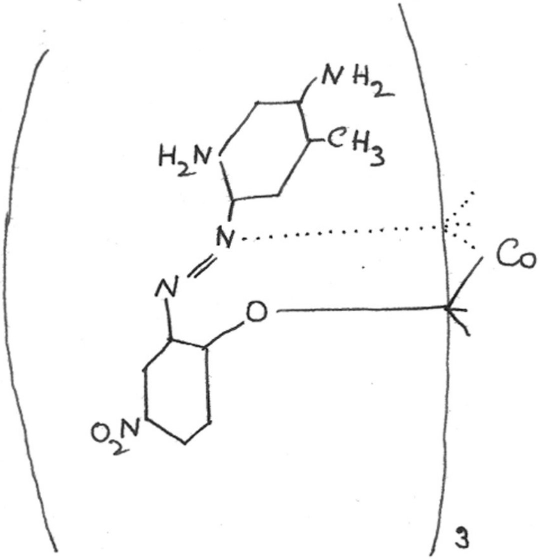
<u>Ortho-o'-dihydroxyazo dyes:</u> Morgan and Smith isolated a number of lakes of this type of dyes. Of these the more important were



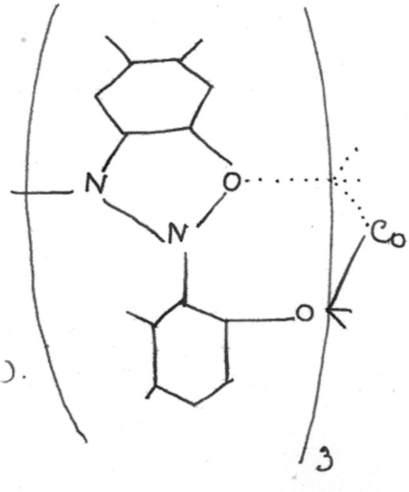
and the complex lake





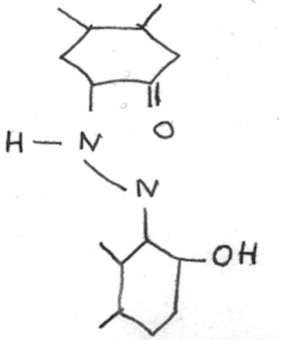


Monohydroxy derivatives have too feeble a lake forming tendency to yield lakes with cobaltammine reagents. The dihydroxy derivatives on the other hand yield stable lakes and are in this respect remarkably unlike the former, hence an alternative formulation



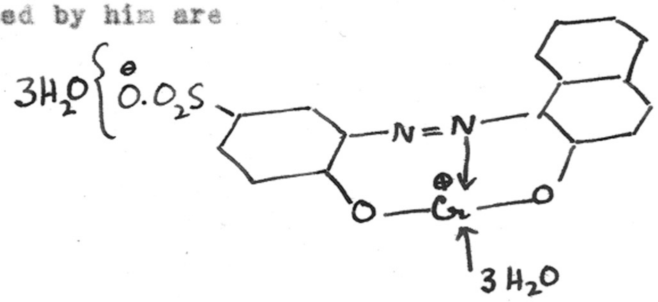
J.C.S. 1924.
P. 1731.
(Morgan & Smith).

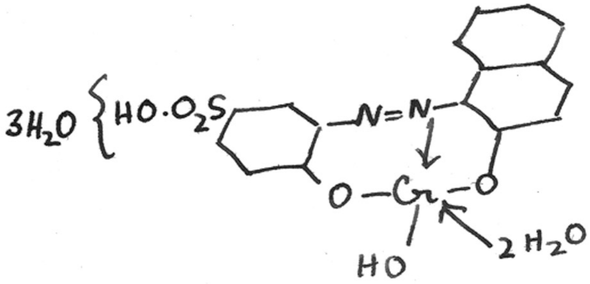
derived from the tautomeric structure

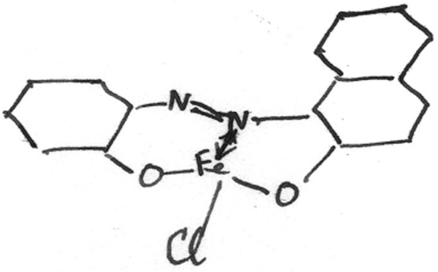


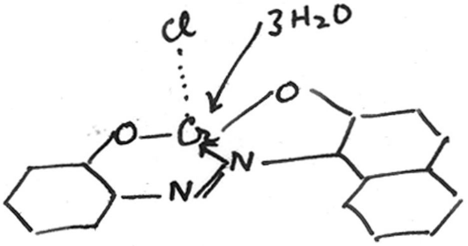
where the feebly acid -NH group also co-ordinated with the cobaltammine, was suggested by Morgan.

Drew (*loc. cit.*) has isolated compounds not formulated by other investigators as yet. Among the types isolated by him are

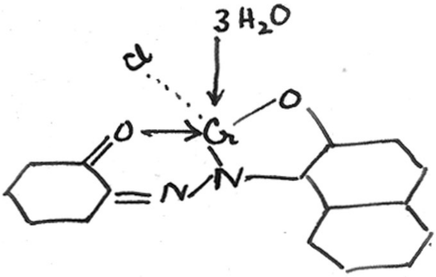




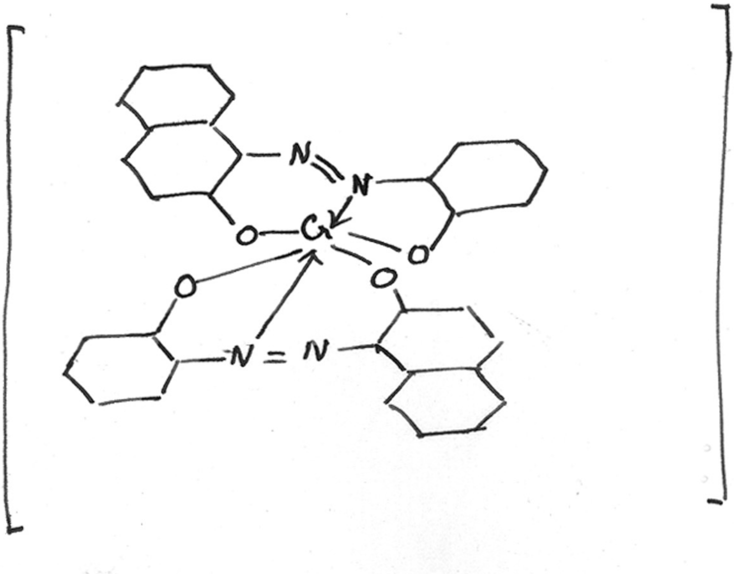




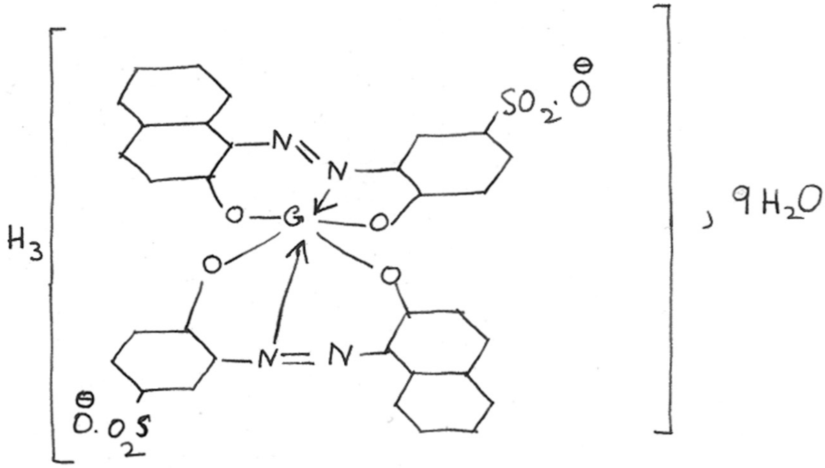
, H_2O

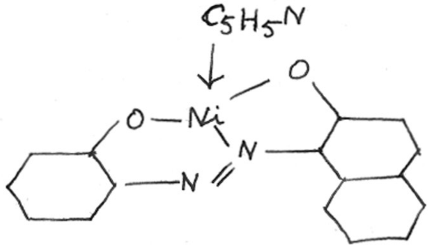


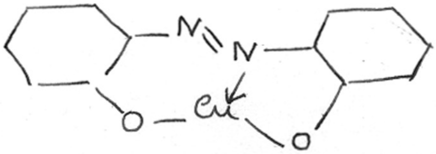
, H_2O

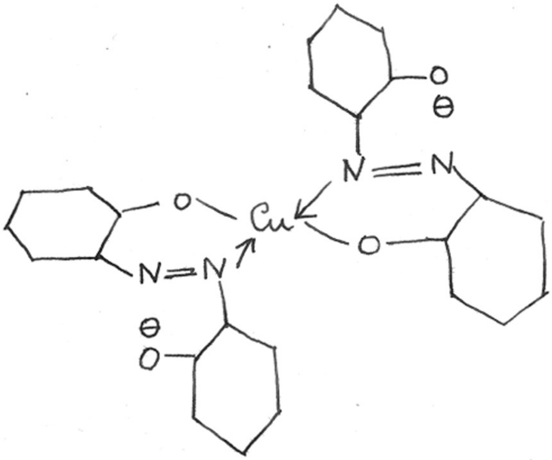


H


H3
SO2·O
N
N
O
G
O
O
O
N
N
O.O2S
, 9 H2O

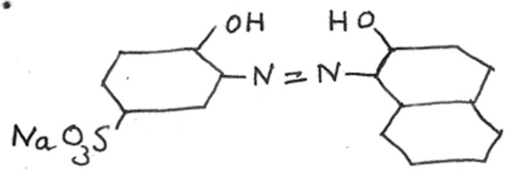

C5H5-N
O
O
Ni
N
N


N
N
O
Cu
O

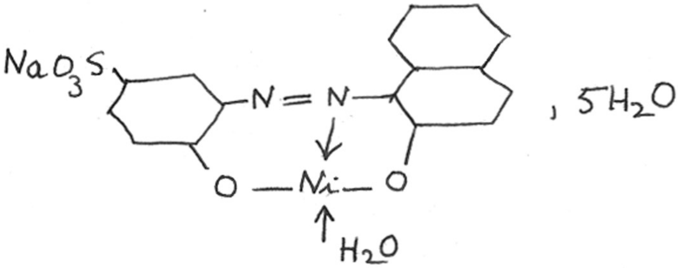


whereas with sulphonic and carboxylic acid groups in the dye it is a general rule that copper does not form the inner complex unless the acid groups are neutralised by copper atoms or basic groups, the free phenolic "OH" groups nevertheless do not prevent the formation of the inner complex salts. The co-ordinatively unsaturated coppe and nickel lakes are the first of their kind isolated by Drew and his collaborators. The co-ordinative unsaturation arises out of the fact that only nitrogen from the azo group is co-ordinatively linked to the metal atom (vide Drew and Landquist, J. Chem. Soc., 1938, 292)

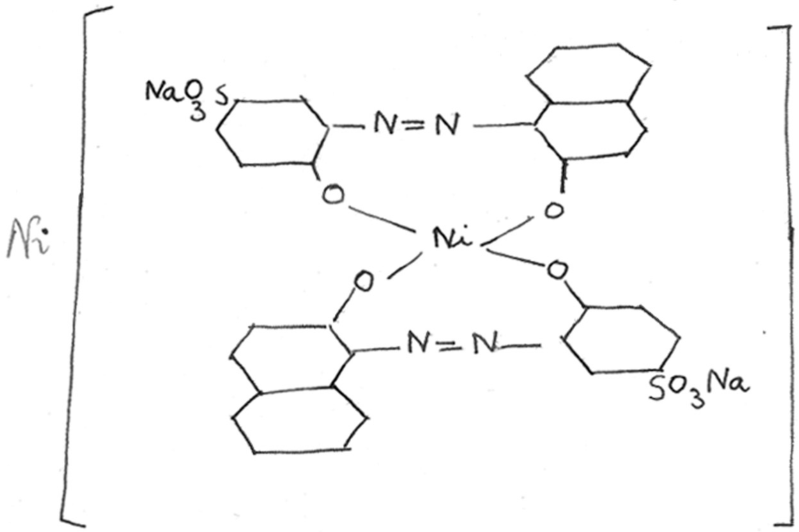
2'-Hydroxy-4'-sodiumsulphophenyl-azo-2-naphthol - Chrome Fast Violet B:



The nickel lake obtained from the molecular proportions of the dye and a nickel salt was of the form

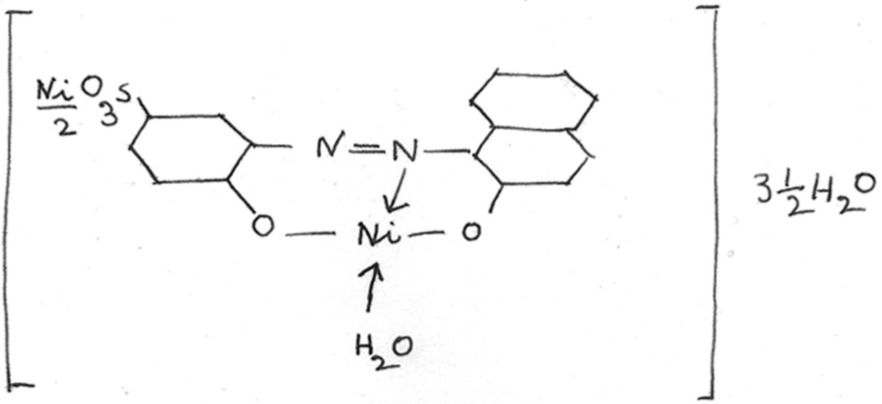


The nickel lake is readily formed, the water of crystallisation can be completely driven off by drying the lake at 160°C., but is regained on keeping in air. An alternative formula might be suggested, where the nickel has no co-ordinating linkage with an azo nitrogen



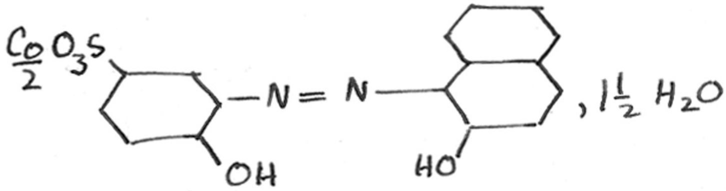
but such a nickel atom being only salt forming, must be ionised and give the tests for the nickel ion with the usual analytical reagents, which is observed to be not the case. Hence the second formulation is not tenable.

A nickel lake containing 1 1/2 atoms of nickel per molecule of the dye was also isolated. It did not contain sodium and was of the form



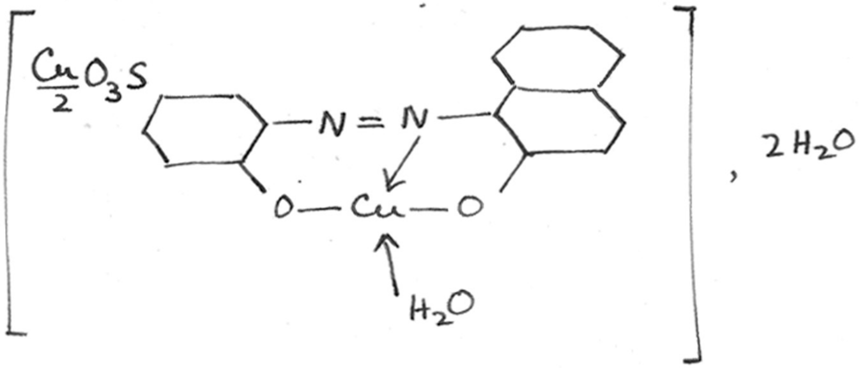
which lost all the water of crystallisation at 160°C., but regained the entire amount when kept in air. In this lake the nickel associated with the sulphonic group was not replaceable by barium, while the nickel attached to the sulphonic group of Chrome Fast Yellow 5G was easily replaced by barium.

With a large excess of a cobalt salt (sulphate, nitrate) the dye gave a simple salt. It would therefore appear that cobalt does not have a characteristic lake forming tendency with this dye, unlike nickel, copper, iron and chromium. The cobalt salt isolated was of the form



in which the cobalt was divalent. This fact that cobalt is divalent only in its simple salts has been confirmed in the various preparations of lakes during the present investigation.

The copper lake was prepared from an aqueous solution of the dye and an excess of a copper salt (sulphate). The product dried at 100°-105°C. was of the form



from which the 2 molecules of water are lost at 160°C., but the 3rd molecule is tenaciously retained.

Catechin: Catechin occurs in catechu in admixture with varying quantities of catechu-tannic acids, and japanic acids. It is isolated from the parent substance by extracting the powdered catechu, evaporating the solution dissolving the residue in water and allowing to crystallise. The resultant product is dissolved in boiling water lead acetate solution added till no more precipitate is formed, and then filtered. The filtrate is digested with hydrogen sulphide to remove lead, and the catechin crystallised from the filtrate in colourless needles. The catechin differs in m.p. and other physical properties depending on the nature of the parent catechu (Thorpe Dictionary of Applied Chemistry - Supplement, Vol. I, 1934,

p. 259; Perkin and Everest, Natural Organic Colouring Matters, 1918 Ed., p. 436).

The nickel lake of the dinitroso derivative of the substance has been isolated; but investigation on this subject is still in progress.

Synthesis of some iron oxide colours from the reduction sludges of aromatic nitro compounds: The iron oxides are among the most popular of the cement colours (*vide* Kudva, *loc. cit.*). The iron oxides provide shades of excellent fastness properties, ranging from yellow, orange and red to deep maroon, brown and black.

The sludge of iron oxide obtained by the reduction of aromatic nitro compounds by means of iron is a valuable black pigment, which gives quite a range of shades on igniting at various temperatures. The resulting amino compound is usually an intermediate for the manufacture of dyestuffs; the most important technical reduction of this type is the reduction of nitrobenzene to aniline. Our country is fast industrialising and the dyestuff industry will naturally occupy the front rank among the "synthetic chemicals" industries. A day will come in the very near future, when quite considerable quantities of the iron oxide sludge will have to be dedisposed of. It was with a view to find an outlet for this "sludge" that the possibility of its use as a cement colour was investigated.

The literature on the subject is rather limited and naturally most of it is not in the form of academic investigations but as patent literature.

B.P. 263,376 describes the production of aromatic amino compounds from the corresponding nitro compounds by reducing them with iron in presence of an inorganic acid such as hydrochloric acid. The addition of aluminium as a salt or as the metal itself gives a yellow sludge which on calcination yields a red oxide. Budinkow (Chem. Zeit., 1928, 52, 846) suggests washing of the magnetic iron oxide sludge obtained in the manufacture of aniline and α-naphthylamine before heating it at 500°-600°C. The oxide, after heating, is ground and gives a brown coloured pigment. But if the sludge were treated with 40% of its weight of an aqueous solution of sulphuric acid (70%) and heated for 2 hours at 750°-800°C., the colour and covering capacity are greatly improved. The higher the temperature of ignition the darker the colour. The stronger the acid used, the lighter the colour. Mixtures with gypsum and heavy spar can be used as in the usual production of ferric oxide colours. Fr. P. 653,226 specifies the production of a ferric oxide, which is suitable as a pigment, by reduction of aromatic nitro compounds by iron and an acid, in presence of difficultly soluble basic salts of tervalent or quadrivalent metals such as aluminium, cerium, thallium, and lanthanum. U.S.P.1,774,932 mentions the use of aluminium chloride with the iron for reduction of nitro compounds, whereby a sludge suitable for use as a pigment is obtained after preparatory treatment, drying and calcining. U.S.P. 1,774,930; and 1,774,931 refer to the production of oxide pigments from the reduction sludge of nitrobenzene. Aluminium either as metal or as its chloride, is also used along with iron. U.S.P. 1,793,942 and 1; 1,793941 refer to the use of the reduction sludge as a pigment. In U.S.P. 1,857,557 is described the production of pigments from the oxide sludge obtained by the reduction of aromatic nitro compounds by iron metal in the presence of a suspension of very finely divided hydroxide or slightly soluble basic salt of a tervalent or quadrivalent metal. The sludge is yellowish brown to brown violet and, if red shades are desired, the sludge is to be subjected to a preliminary calcination. U.S.P. 1,849,428 also refers to the production of pigments from the oxide sludge obtained by reduction of the nitro compounds by uss iron in presence of a small quantity of hydrochloric acid and a sufficiency of sodium chloride in solution. U.S.P. 1,837,709 mentions the preparation of ferrous sulphate from the aniline sludge by treating it with sulphur and sodium chloride, and the resulting ferrous sulphate is calcined to produce ferric oxide, and the oxide is pulverised. U.S.P. 1,835,409 specifies the use of dilute aqueous solution of the acid containing a salt of a rare earth metal, such as cerium chloride in quantity insufficient to dissolve the iron. The oxide pigment obtained is improved thereby. In B.P. 275,562 and 279,283 it is claimed that a compound of lead (such as lead oxide or lead carbonate) should be employed together with iron powder for the production of pigments of good quality. Very good iron reds are obtained by treating the iron sludge with an amount of sulphuric acid substantially less then the chemical equivalent of it (U.S.P. 1,943,948). The final pigments (after calcining) are stated to be good reds. U.S.P. 1,998,540 and 1,998,541 exploit the fact that lead compounds when present in the solution of nitrobenzene during reduction with iron gives a sludge which yields bright "reds" on calcination. U.S.P. 1,979,597 suggests the grinding of the aniline sludge with calcium hydroxide and then calcining. A method of preparing an oxide pigment is to mix the black oxide (aniline sludge) with sulphuric acid or ammonium sulphate and then to calcine the product in admixture with a chloride of ammonia, iron, calcium, barium or strontium (U.S.P. 2,105,670).

The preparation of oxide colours from the reduction sludges of nitrobenzene and 4-nitrotoluene-2-sulphonic acid has now been examined, and the effect of the addition of other metals in the metallic state or in the form of their salts has also been studied. The results show that no remarkable modifications in shade for fastness of the final pigment are achieved by addition of other metals in any form.

Cement water-proofing agents: In recent years a large number of cement water-proofing agents have appeared in the market. As yet, however, few attempts have been made to produce these compounds in our country in spite of the obvious demand for them. In general, coloured cements are rendered water-proof also by addition of these compounds. Owing to the very large number of these materials being available, it would seem advisable to test their efficacy before indiscriminately using them. For this purpose an apparatus for measuring the permeability of cement or cement concrete to water has been designed. But on account of the war the spindle valves, which were an essential part of the apparatus were not obtained in time to and no tests could be taken on the apparatus.

The object of using water-proofing compounds is to render cement concrete more impervious to the passage of water. In consequence the use of these compounds is confined largely to dams, water storage tanks, tunnels, etc., where the concrete is exposed to a hydrostatic head.

These compounds may be liquids of various consistencies and may be solid powders or pastes. Lea and Desch (Chemistry of Cement and Concrete, 1937 *Ed.*, 351) have classified them as under: (1) Inert materials acting as pore fillers such as hydrated lime, clays, ground silica, silicates, talc (soap-stone), chalk, barium sulphate, etc. (2) Active materials acting as pore fillers, such as sodium and potassium silicates, silicofluorides, iron filings with ammonium chloride, and diatomaceons silica. (3) Soluble chlorides and sulphates such as calcium and aluminium chlorides, alum, alkali sulphates and gypsum. These materials may all be regarded as active additions which in some cases also act as pore fillers. (4) Inert water repellent materials such as calcium soaps, waxes, mineral oils and jellies, bitumen, coal tar residues, glue and cellulose with wax in ammoniacal copper solution. (5) Active water repellent materials, such as sodium, potassium and ammonium soaps, free fatty acids, vegetable oils and resins.

The materials classed as active are those which react in some way with the cement.

Lea and Desch do not consider it necessary to use these compounds, as according to these authors laboratory tests have not shown the remarkable attributes often referred to them. It seems likely, in spite of what has been said, that the chemist will be able to synthesise some compounds which will very considerably decrease the permeability of concrete to water under the most drastic conditions.

A large proportion of the literature ofon the subject of water-proofing of cement is in the form of patent literature. The majority of the patents refer to the use of soaps, as for example, <u>Jap. P.</u> 40,198; <u>U.S.P.</u> 1,437,893; 1,471,410; 1,550,355; 1,589,650; <u>B.P.</u> 240,396; <u>U.S.P.</u> 1,565,125; <u>B.P</u>. 247,947; 247,976; <u>Jap. P.</u> 69,075;

B.P.322,182; U.S.P.1,749,923; B.P. 317,902; U.S.P. 1,803,557 1,814,292; 1,737,006; 1,779,481; B.P. 344,025; 357,119; 391,582; U.S.P. 1,886,379; Ger.P. 560,447; Fr. P. 758,641; B.P. 428,192; U.S.P. 2,008,034; 2,003,613; Ger. P. 618,781; Fr. P. 786,631; U.S.P. 6182,019,980; B.P. 460,736; Ger.P. 634,761; Russian P. 29,399; Fr. P. 818,118; Swiss P.178,473 All make use of a soap as the active water-proofing agent. It would therefore appear that soap in some form is very popular cement water-proofing agent.

Rather a novel method suggested for rendering concrete impervious to fluids is to heat it up to a temperature of about 200°-205°C., to drive off part of the water of combination and then to fill up the voids (U.S.P. 1,383,749).

The use of inert water"repellents" in some for of other is mentioned in a number of patents. The water repellents are bitumen, asphalt, paraffin, waxes and coal tar residues or their aqueous emulsions. Among the earlier patents is U.S.P. 1,382,988, which mentions the use of paraffin in conjunction with slaked lime. Other patents on the subject include U.S.P. 1,402,412; 1,505,112; 1,539,193; 1,566,498; B.P. 250,852; U.S.P., 1,721,861; Swiss P. 127,975; U.S.P. 1,772,999; 1,755,638; 1,752,214;

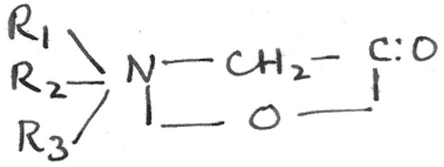
B.P. 319,288; U.S.P. 1,738,022; 1779,481; 1,864,942; Ger.P. 579,386; U.S.P. 1,913,430; 1,906,276; 1,912,626; B.P. 410,479; Swiss P. 166,135; Australian P.13,953; 13,933; Ger. P. 604,340; U.S.P. 2,067,772;
All of these employ repellents, either alone or in conjunction with other materials.

Other means employed usually are the use of the salts such as calcium chloride, magnesium chloride, sodium silicate (water glass) and calcium hydroxide (slaked~~)~~ lime). Mention may also be made of iron used in conjunction with ammonium chloride. Under the circumstances the iron rusts quickly and gives a voluminous rust which fills up the voids and renders cement water-proof. B.P. 156,621 employs colloidal (freshly precipitated) calcium silicate. U.S.P. 1,415,324 makes use of an alignate such as that formed by the action of ammonium alginate on cement. U.S.P. 1,396,546 specifies the use of finely ground burnt clay saturated with sodium silicate with a small amount of magnesium sulphate. Swedish P. 52,563 employs pulverised bricks or talc. According to Can. P. 226,350, concrete is made water-proof by the addition of diatomaceous earth. U.S.P. 1,506,193 mentions the following water-proofing composition - Plaster of Paris 1, wood fibre 1, cement 2 and hydrated lime 0.5 parts. A mixture of white copperas, glue, water gives a water-proofing composition (B.P. 200,564). Can. P. 247,397 gives a composition containing a water repellent material and lime, a mixture of water absorbing halogens and a metal carbonate. U.S.P. 1,530,533 employs a colloidal solution of calcium silicate, calcium carbonate emulsified with a soap. The use of powdered silica in aqueous solution of water glass is covered by B.P. 256,258. The use of calcium chloride and magnesium chloride in conjunction with shale, slag or slate is covered by B.P. 244,603. A special water and acid-proof cement compound is obtained by mixing a powder containing such substances as tungstic acid, salts of fluorozinconic acid, flourogermanic, flouric, flourotitanic, flourotantalic, flouroni~~ll~~obic and flourostannic acids, silicon, silicon alloys, flousilicates, cryolite or aluminium (B.P. 283,471).

Protection is granted to the use of a pulverised alloy of silicon instead of silicon with magnesium, calcium, aluminium or iron in water glass (B.P. 281,689). The use of a composition comprising alum and a solution of shellac which may be ~~s~~in alcohol acetic acid, soda, borax or potash to form a pasty mixture is specified in B.P.281,022

B.P. 301,509 takes advantage of the use of hydrochloric acid or chlorides, such as those of calcium, aluminium, titanium, tin and iron for water-proofing. B.P. 291,988 again specifies the use of chlorides and flourides, together with other materials. Ger. P. 502,017 covers the use of kieselguhr, asbestos or like insulating materials, together with coal tar. Belg. P. 366,022 suggests addition of a fatty acid, together with a number of other compounds. Casein can also be used. (Can. P. 302,237). Freshly precipitated alumina and boric acid are employed (B.P. 325,991). Metal dust, together with ammonium chloride gives good water-proofing qualities (B.P. 318,285). Metal sulphates can render the concrete structures water-proof (B.P. 310,875). Gelatinous materials, such as glue, a soluble or partly soluble silicate or fluosilicate are sometimes employed (Ger. P. 553,360). A water-proofing mixture of barium sulphate, quick lime, silica acid, soluble glass, aluminium silicate is claimed under Fr. P. 727,942. Iron filings and ammonium chloride (U.S.P. 1,825,199), alkali aluminates (Fr. P. 705,920), pulverised limestone and ammonium chloride (Swed. P. 69,367) are all mentioned in the literature as having cement water-proofing qualities. B.P. 355,902 mentions that the clinker on treating with ammonium or sodium phosphate, or flourine will acquire greater resistance to water. Austrian P. 136,398 claims that cement compositions are improved in their mechanical properties and resistance to water by addition of up to 2.5% of a protein and up to 12% of an alkaline earth oxide or hydroxide calculated on the dry cement. Swed. P. 76,932 claims that a composition consisting of rubber, fat and wood tar with rubber as the main substance decreases the permeability of concrete. According to U.S.P. 1,995,963 about 0.008 - 0.015% of a soluble alkali metal soap, soluble organic soap such as a triethanolamine soap, soluble salt of sulphonated hydrocarbon oil is added. According to Fr. P. 791,359, compounds soluble in water containing at least 8 carbon atoms in the molecule, but not containing SO_3H group are added to cements to obtain cements specially light to water. Compounds including polyethyl alcohol of lanolium sodium abietate, oxyethylated fatty acid of spermacetic oil, oxyethylated dodecyl alcohol, oxyethylated casein, poly oxyethylated oleic alcohol, oxyethylated methyl cyclohexanol, oxyethylated ricinoleic acid, oxyethylated, xylenol, cresol polyglycolic ether, stearyl aminopolyglycolic oxide and oxyethylated octadecylic alcohol, are cement water-proofing agents. Fr. P. 790,420 claims that silicious materials, when finely ground and used in conjunction with sodium silicate, calcium hydroxide or sodium flouride, render the cement water-proof. B.P. 466,639 describes the addition of a water soluble derivative of lignin to hydraulic cement -aggregate-water concrete mixture. The derivative may be tricalcium lignin sulphonate, lignin salts formed by replacing all or part of the combined calcium in sulphonate with hydrogen alkali metal or ammonia or by treating the sulphonate with sulphur-dioxide, sodium lignate, separated from "black liquor" and purified, the sodium salt of the condensation product of lignin and (1) glycerol monochlorohydrin or (2) ethylene glycol, chlorolignin, or phenol derivative of lignin. Methods of preparation of these derivatives are described. Ger. P. 648,056 refers to the use of sodium silicate along with certain other compounds while B.P. 460,366 specifies the use of such water soluble organic compounds as containing in the molecule at least 15 carbon atoms and 2 or more aromatic nuclei attached to a heterogeneous nucleus that contains elements other than carbon, hydrogen, e.g. nitrogen will peptise ~~hydrogen~~ hydraulic cement particles and disperse them uniformly throughout a mixture. Belg. P. 413,484 mentions the use of a mixture of aluminium and zinc salts.

A cement mixture is prepared containing about 0.5 to 2% of dodecyl betaine or other betaine of the formula



where R_1, R_2, R_3 stand respectively for high molecular alkyl radical~~s~~ and for low alkyl radicals (R_2 and R_3) (U.S.P. 2,131,533). B.P. 470,365 specifies the grinding of cement clinker in presence of a water soluble hydroxy alkylamine, or a salt or a derivative thereof, e.g. triethanolamine or tri-isopropanolamine or a salt thereof.

H.L.Kennedy (Ind. Eng. Chem., 1936, 28, 963) has exhaustively studied the effect of catalysis and dispersion on Portland cement. The catalyst employed was cement compound TDA. Among the advantages of the use of this compound is also mentioned the increased impermeability to the passage of water.

In general the "repellents" possess very good waterproofing qualities; but as integral water-proofers their use is not to be encouraged. These compounds "enclose~~d~~" particles of cement and prevent the normal dispersion of cement particles in the gauging water, which results in the drop of the ultimate strength of the cement concrete. In addition these compounds produce segragation of cement particles. The soaps and the various synthetic organic compounds will find greater use as cement water-proofers than these 'repellents'.

Two commercial cement water-proofing agents have been analysed in the present work. They are essentially calcium soaps of stearic acid, and contain a very large percentage of hydrated lime.

EXPERIMENTAL

Standardisation of the fastness properties of coloured cements: The deciding factor in the use of coloured cements, apart from their cost, being their fastness properties, a fastness standard for coloured cements was evolved similar to the one for textiles developed by the German Fastness Committee, the Society of Dyers and Colourists (Report of the work of the Fastness Committee in fixing standards for light, perspiration and washing, 1934), and the American Association of Textile Chemists and Colourists (American Association of Textile Chemists and Colourists, 1937 year book, p. 94); these methods for textiles have recently been submitted to fresh scrutiny in this laboratory (cf. R. V. Bhat, *M.Sc.Tech. Thesis*, University of Bombay).

Fastness to light: Fastness to light of coloured cements was classed into 8 grades depending on the number of hours of exposure in the Calico Printers' Association Fadeometer required to bring about a distinct alteration in shade of the exposed sample. The C. P. A. fadeometer consists of a carbon arc lamp, with a water jacket of glass surrounding it. By this means the temperature in the device can be kept sufficiently low. There is a fan with the blades secured horizontally mounted under the lamp over a water trough. By varying the speed of the fan, the humidity could be controlled. The samples are mounted in a circle round the lamp. The samples for exposure were prepared by gauging the coloured cements with 24% of their weight of water, kneading well and filling them up in circular tin boxes of 1 1/4" diameter and 2/5" thickness. The suffece was smoothed over with a spatula; a tin lid covering only half the surface was then put on and the exposure to light continued from the next day onwards. The graded standards of fastness to light were adopted from the previous experience with various pigments used as cement colours (Kudva, M.Sc.Tech. Thesis, University of Bombay, 1939). The coloured cements selected as standards were so chosen on account of the convenient intervals of hours for fading of the colour between one grade and the next.

Grade 1: One percent (by weight) Lake Fast Red No. 541 (J. W. Leitch and Co. Ltd.). The coloured cement was prepared by grinding 100 g. of white Portland cement with 1 g. of the lake in a porcelain mortar until a uniformly coloured cement was obtained.

__Grade 2:__ 10 Ten per cent. of Malachite Green Lake on Green Earth. The lake was prepared in the manner described earlier (__loc. cit.__). The coloured cement was prepared as for Grade 1.

__Grade 3:__ 0.5Half per cent Hansa Yellow 5GL (I. G. Farbenindustrie).

__Grade 4:__ Ten per cent of Methylene Blue BB lake on Green Earth (__loc. cit.__).

__Grade 5__: Half per cent Indanthrene Brilliant Green 4G. 0.125 G. of the dye, 1.1 c.c. of 4% sodium hydroxide and 0.25 g. of hydrosulphite and 6.8 c.c. of water were warmed to 60°C. and cooled to room temperature. 25 G. of cement were then gauged with this vat, kneaded well and moulded into the exposure boxes.

__Grade 6:__ Two per cent Pigment Fast Red PRNL (J.W.L.).

__Grade 7__: "Aquamarine Cement" (Associated Portland Cement Manufacturers, England).

__Grade 8__: Half per cent Monastral Fast Blue BS.

The exposure boxes were mounted on special frames prepared for the purpose, so that wenwhen mounted on these frames vertically the light of the C.P.A. fadeometer lamp could play fully on the surface. The humidity of the atmosphere could be controlled fairly well by regulating the speed of the fan. The intensity of the light was maintained reasonably uniform by keeping the length of the arc constant at 1 1/2". As only one half of the samples were exposed, fading due to the effect of light would take place only in the exposed portion. Every two or three hours the samples were examined by carefully opening the lid and observing whether there was any difference in depth or tone between the exposed and unexposed parts. At the least sign of such an alteration further exposure was discontinued, and the number of hours required to bring about the change noted. Following are the results, i.e. number of hours required to bring about "fading" at maximum temperature 46°C., minimum temperature 42°C., and humidity 80%.

Grade	Time in hours
1	5
2	10
3	17
4	23
5	50
6	71
7	96
8	120

With these results as the basis any sample fading under 10 hours was considered Grade 1, above 10 hours, but below 17 Grade 2, above 17 hours, but below 23 Grade 3, above 23 hours, but below 50 Grade 4, above 50 hours, but below 71 Grade 5, above 71 hours, but below 96 Grade 6, above 96 hours, but below 120 Grade 7, and above 120 hours Grade 8.

Fastness to washing was graded into 5 classes following textile practice. For determining this property for Grades 1 to 3, 25 g. of the cement were agitated with 100 c.c. of water in stoppered glass bottles, agitation being secured by a mechanical shaker. At the end of 30 minutes the bottles were removed, and the contents filtered off and examined. Grs Grade 1: complete destruction of colour: Ten per cent (by weight) lake of Auramine O on Green Earth. The colour of the cement was completely destroyed.

Grade 2: alteration of shade: Half per cent Lake Fast Red No. 541 (J.W.L.). The shade was altered from red to orange, and there was slight bleeding.

Grade 3: no alteration in shade: There appeared no alteration in shade, but there was slight bleeding of the Aquamarine coloured cement.

Grades 4 and 5: Slight bleeding in boiling water and no bleeding respectively. 25 G. each of 'special yellow cement' and 'blue cement' ra were boiled in 100 c.c. of water with agitation for 30 minutes, then filtered off. If the coloured cement had bled as indicated by the coloured filtrate, it was graded 4, otherwise 5. The gradation could, therefore, be summarised as follows:

1 Complete destruction of colour.
2 Alteration in shade with without bleeding.
3 No alteration in shade but slight bleeding.
4 Slight bleeding in boiling water, but no other change.
5 No change, and no bleeding.

Fastness Properties of Coloured Cements

I. Naphtol dyes on cement: The solutions of the Naphtols were prepared according to the "cold process" by dissolving in the requisite amount of methylated spirit and 62°Tw caustic soda solution, and the Naphtol solution brought to the required concentration. The calculated amount of the diazo salt dissolved in water was then coupled with the Naphtol. The resultant dye was filtered and washed with water, then with dilute alkali solution (1% caustic soda), followed by 1% dilute hydrochloric acid. Dyes were similarly obtained by coupling anacardic acid and

2:3-hydroxynaphthoic acid respectively with diazo salts. The following dyes were pa~~p~~prepared and used: Dyes from Naphtol AS and Red Salt ~~TR~~ TR, Naphtol AS and Fast Blue Salt BB, Naphtol AS and Scarlet Salt GG, Naphtol AS-G and Fast Scarlet Salt GG, 2:3-hydroxynaphthoic acid and Fast Red Salt TR, Naphtol AS-G and Fast Red Salt TR, Naphtol AS-E and Fast Red Salt TR, Naphtol AS-BO and Fast Red Salt TR, Naphtol AS-TR and Fast Red Salt TR, Naphtol AS-RL and Fast Red Salt TR, Naphtol AS-ITR and Fast Red Salt TR, tetrahydroanacardic acid and Fast Red Salt TR, Naphtol L3G and Fast Red Salt AL, and Naphtol AS-ITR and Fast Red Salt AL.

The dye thus prepared in substance was then ground up with white Portland cement and the coloured cement was gauged with 24% of its weight of water, kneaded well and filled up in circular tin boxes as described earlier.

For determining the fastness to washing, 25 g. of the coloured cement were treated as indicated before.

The cement was dyed with azo dyes derived from anacardic acid as in the case of azoic dyes derived from Naphtols on textiles. The cement was pasted up with the acid solution in the requisite amount of methylated spirits and 62°Tw caustic soda solution; the gauging water was a solution of the calculated amount of the diazo salt. In this process, as a large amount of heat was evolved during gauging, the solution of the diazo salt in ice was employed.

II. <u>Substantive dyes:</u> These were applied by dissolving the requisite amount of the dyes in the gauging water. Uniform shades were obtained, and they were also very bright. The following dyes were employed: Sirius Supra Green BL, Sirius Supra Blue 6G, Sirius Supra Scarlet B.

III. <u>Metal co-ordinated azo dyes:</u> These dyes containing either chromium or copper in the dye molecule were applied in a similar manner to the substantive dyes. The shades obtained were rather dull.

With a view to increasing the fastness of these dyes when employed as cement colours, it was considered worth examining the use of casein, dyed with these dyes as a cement colour. Casein being a protein is dyed by the Neolan and Palatine Fast colours in the same manner as wool and silk. The casein thus dyed was ground up with cement as usual.

33 G. of casein suspended in 500 c.c. of a 0.2% solution of the dyestuff, and 2.6 c.c. of concentrated sulphuric acid was slowly brought to the boil and refluxed for 3 hours, at the end of which the mass was allowed to stand.

On cooling, the casein was found to be deeply coloured and the supernatant ~~colour~~ solution had but a faint colour, the dye bath being almost completely exhausted. Filtration was difficult as the casein had gelatinised. The following dyes were used in this manner: Palatine Fast Blue GGN, Palatine Fast Green GN, Neolan Blue GG.

IV. Alizarine Lakes: Lakes of alizarine were prepared as follows:

Aluminium lake: Aluminium sulphate (20 g.), corresponding to 3.6 g. of alumina was dissolved in the least amount of water. Alizarine (3 g.) was dissolved in an aqueous solution of ammonia and then added to 10 g. of lead sulphate mixed with sufficient water and 25 g. of blancfixe paste. The lake was precipitated ~~canby~~ by addition of 40 g. of phosphate of soda dissolved in 400 c.c. of water. The lake was washed well, filtered and dried. The lake, a bright bluish red, was ground up with cement as usual.

Iron lake: The following method proved quite satisfacotry for the production of the iron lake.

Ferrous ammonium sulphate (7 g.) was dissolved in 200 c.c. of water. To this was added 20% alizarine paste (20 c.c.), dissolved in 5 c.c. of liquor ammonia, and 100 c.c. of water. The reaction mixture was boiled for about 2 hours, filtered off, washing the precipitate with hot water. The filtrate was greenish yellow. The precipitate was dark purple.

Nickel and vanadium lakes: These were similarly prepared. They were violet and purple in colour respectively.

Tin lake: This was prepared as follows: 2 G. of stannous chloride in 100 c.c. of water and 1 g. of calcium chloride in 50 c.c. of water were added to 4 g. of alizarine dissolved ~~a~~in ammoniacal solution of water. The reaction mixture was boiled for 2 hours, and filtered. The lake was bright red.

In addition alizarine was employed for colouring cement by gauging cement with an ammoniacal solution of alizarine. The lake was formed by interaction with the cement, but the shade was not uniform. Alizarine Saphirol R and Alizarine Irisol R were applied by emulsification with Turkey Red oil. The dye (0.5 g.) was pasted up with Turkey Red oil and 100 g. of cement was guaged with the addition of 23 c.c. of water and exposure samples were prepared as usual.

V. Anthraquinone vat dyes: The dyes had very poor covering power when ground dry with cement, and as much as 5% of the dye was required to produce a sufficiently deep shade. It was, therefore, applied in the vatted form with a slight modification of the process as applied to textiles. The amounts of hydrosulphite and caustic soda taken were the same as in the dyeing of textiles, but Glauber's salt and common salt were not employed even in the case of the IK or cold dyeing colours. For example, Indanthrene Green GG was applied as follows: 0.125 g. of the dye, 1.1 c.c. of 4% sodium hydroxide and 0.25 g. of hydrosulphite and 6.8 c.c. of water were warmed to 60°C. and cooled to room temperature. 25 G. of cement were then gauged with this vat, kneaded well and moulded into the exposure boxes as usual. The following dyes were used in this manner: Indanthrene Brilliant Green GG, Indanthrene Brilliant Green 4G, Indanthrene Blue GCD, Indanthrene Brilliant Pink R, Indanthrene Brilliant Green B and Indanthrene Violet BN.

VI. Lakes of quinone-oximes: Among the lakes of the nitroso phenol (or quinone-oximes) type, (methods of preparation given later), the iron lakes obtained from the 1-nitroso derivative of Naphtol AS gave with 0.5% of the colour on the weight of the white Portland cement a sufficiently deep green shade. The shade was deeper than that obtained with corresponding quantities of the chromium —

oxides. The fastness to light was 8, and to washing 5. The cobalt lake gave a pleasant red with just 0.5% of the colour on the weight of the cement. It also showed equally excellent fastness properties. Nickel and copper lakes also gave similar results. The following lakes were examined: 3 iron lakes, cobalt, nickel and copper lakes, and iron and copper lakes of the nitroso derivative of Naphtol AS-GR.

VII. Iron oxides: The dark (almost black to black) sludge of iron oxide obtained from the reduction of nitrobenzene and 4-nitrotoluene-2-sulphonic acid provided a very fast black pigment. The oxides of various shades obtained by ignition of the sludges, were pigments of the highest fastness properties.

VIII. Commercial pigments: The following 15 commercial pigments were examined and were mostly found to be inorganic:

1. Cement red (I.C.I.) essentially an oxide of iron
2. Cement yellow (I.C.I.) " " "
3. Cement green (I.C.I.) " " chromium
4. Cement blue (I.C.I.) Ultramarine Blue
5. Cement blue (I.C.) A manganese blue. The cement blue dissolved completely in boiling concentrated sulphuric acid, giving a pale purple solution, whichoon

cooling and diluting gave a pale pinkish solution and a slightly brownish precipitate. The pigment became greener on igniting strongly (1000°C.). Fused with sodium peroxide the melt was green which gave on leaching with water a brown mass. Qualitative tests showed the presence of large quantities of barium and sulphate and a comparatively smaller quantity of manganese. Other metals were absent. The pigment gave on analysis barium 60.0%, sulphate 36.7% and manganese dioxide 4.1%.

6. Yellow No. 415 (I.G.) essentially an oxide of iron
77. Yellow No. 460 (I.G.) " " "
8. Chromium Oxide Green G - chromium oxide
9. Iron Oxide Red 510 (I.G.) - iron oxide
10. Iron Oxide Red 140F(I.G.) - " "
11. Iron Oxide Red 520 (I.G.) - " "
12. Green (Bharat Tiles) - chromium oxide
13. Yellow (" ") - iron oxide
14. Red (" ") - " "
15. Blue (" ") - organic lake on blanc-fixe base

Table I

Fastness properties of coloured cements

No.	Percentage	of pigment from	Fastness to light	Fastness to washing
1	0.5	Naphtol AS + Red Salt TR	1	5

Table I contd.

No.	Percen-	Pigment from	Fastness to	
			light	washing
2	0.5	Naphtol AS + Blue Salt BB	1	5
3	0.5	Naphtol AS + Scarlet Salt GG	1	5
4	0.5	Naphtol AS-G + Scarlet SaltGG	1	5
5	0.5	2:3-Hydroxynaphthoic acid + Red Salt TR	1	5
6	0.5	Naphtol AS-G + Red Salt TR	1	5
7	0.5	Naphtol AS-E + Red Salt TR	1	5
8	0.5	Naphtol AS-BO + Red Salt TR	1	5
9	0.5	Naphtol AS-TR + Red Salt TR	1	5
10	0.5	Naphtol AS-RL + Red Salt TR	1	5
11	0.5	Naphtol AS-ITR + Red Salt TR	1-2	5
12	2.0	Tetrahydroanacardic acid + Red Salt TR	2	4
13	0.5	Naphtol L3G + Red Salt AL	1-2	5
14	0.5	Naphtol AS-ITR + Red Salt AL	1-2	5
		Pigment		
15	0.5	Indanthrene Brilliant Green GG	7-8	
16	0.5	Indanthrene Brilliant Green 4G	5	
17	0.5	Indanthrene Blue GCD	8	
18	0.5	Indanthrene Brilliant Pink R	5	

No.	Percentage	Pigment	Fastness to	
			light	washing
19	0.5	Indanthrene Brilliant Green B	8	
20	0.5	Indanthrene Violet BN	7	
		Alizarines		
21	0.5	Alizarine Saphirol R	4	
22	0.5	Alizarine Irisol R	4	
23	1.0	Iron lake of alizarine	1-2	3
24	1.0	Nickel lake of alizarine	1-2	3
25	1.0	Vanadium lake	1-2	3
26	1.0	Tin "	1-2	3
27	1.0	Aluminium "	1-2	3
		Substantive dyes		
28	0.5	Sirius Supra Green BL	1	
29	0.5	Sirius Supra Blue 6G	1	
30	0.5	Sirius Supra Scarlet B	1	
		Azo-co-ordination complexes		
31	0.5	Palatine Fast Yellow GRN	3	
32	0.5	Palatine Fast Green GN	4	
33	0.5	Palatine Fast Blue GCN	4	
34	0.5	Neolan Red R	1	

No.	Percentage	Azo-co-ordination complexes	Fastness to	
			light	washing
35	0.5	Neolan Blue GR	1	
36	3.0	Casein dyed with Palatine Fast Blue GGN (3.3% dye on casein)	4	
37	6.0	Casein dyed with Palatine Fast Green GN (3.3% dye on casein)	4	
38	3.0	Casein dyed with Neolan Blue GG (3.3% dye on casein)	4	
		Nitroso lakes of Naphtol AS		
39	0.5	Iron lake (ferrous)	8	5
40	0.5	Iron lake (ferric I)	8	5
41	0.5	Iron lake (ferric III)	8	5
42	0.5	Cobalt lake	8	5
43	0.5	Nickel lake	8	5
44	0.5	Copper lake	8	5
		Lakes of nitroso derivatives of Naphtol AS-GR		
45	0.5	Iron lake	8	5
46	0.5	Copper lake	8	5
		Oxide colours		
47	One part for 30 of white Portland cement (I.C.I.) cement red		8	5

Table I contd.

No.	Oxide colours	Fastness to light	Fastness to washing
48	1 part cement yellow (I.C.I.) for 75 parts of white Portland cement	8	5
49	1 part cement blue (I.G.) for 10 parts of white Portland cement	8	5
50	1 part of cement yellow No. 415 (I.G.) for 75 parts of white portland cement	8	5
51	1 part of cement yellow No. 460 (I.G.) for 75 parts of white Portland cement	8	5
52	1 part of Chromium Oxide Green G for 15 parts of white Portland cement	8	5
53	1 part of cement green (I.C.I.) for 15 parts of white Portland cement	8	5
54	1 part of iron oxide red (510 (I.G.) for 30 parts of white Portland cement	8	5
55	1 part of iron oxide red 520 (I.G.) for 30 parts of white Portland cement	8	5
56	1 part of iron oxide red 140F (I.G.) for 30 parts of white Portland cement	8	5
57	6 parts of cement green (Bharat) for 100 parts of white Portland cement	8	5

Table I contd.

No.	Oxide colours	Fastness to light	Fastness to washing
58	1 part part of cement yellow (Bharat) for 50 parts of white Portland cement	8	5
59	1 part of cement red (Bharat) for 50 parts of white Portland cement	8	5
60	3 parts of cement blue (Bharat) for 50 parts of white Portland cement	8	5
61	1 part of iron oxide sludge fom (nitrobenzene reduction) for 15 parts of white Portland cement	8	5
62	1 part of iron oxide sludge ignited at 400°C. for 30 parts of white Portland cement	8	5
63	1 ---do---- ignited at 600°C.	8	5
64	1 ---do---- " 800°C.	8	5
65	1 ---do---- " 1000°C.	8	5
	Effect of concentration of azoics on fastness to light		
66	0.5% dye from Naphtol AS and Red Salt TR	1	
67	2% dye from Naphtol AS and Red Salt TR	2-3	
68	5% dye from Naphtol AS and Red Salt TR	5	

In view of the high cost of the anthraquinone vat calour colours and their poor tinctorial power on cement, methods of surface application, e.g. by spraying an emulsion of the dye, were studied. (1) 5% of acetylated cellulose solution, technically called sericose LC, was dissolved in a special solvent known as sericosol N. The anthraquinone pigment containing not more than 25% water was beaten up with a little methylated spirit or sericosol N and then added to the requisite quantity of the 5% solution. Thinning could be done with sericosol N if found necessary. When the dye paste was sprayed on to the cement surface by means of a spray gun, the surface was uniformly and richly coloured, and the fastness to light was as good as when applied as usual. (2) A 10% solution of acetylated cellulose was prepared in sericosol N, to which was added thorough mixing 10% of Indanthrene Printing Blue GG Suprafix. The paint was sprayed as before. (3) The requisite quantity of the dye (Indanthrene Brilliant Green B) was pasted up with Turkey Red oil and diluted with a small amount of water and mixed with British gum thickener and 2% caustic soda of 70°Tw added. 1% of hydrosulphite was followed up after the temperature was raised to 60°C. This was kept at this temperature for 20 minutes and Rongolite C (1 lb. per gal.)

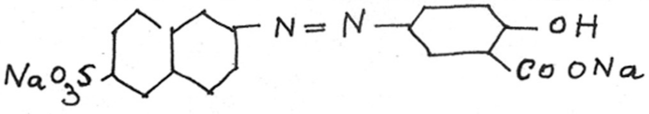
added. Excess of caustic soda was destroyed by addition of sodium bicarbonate. One ~~of~~lb. of glycerine was added per gallon of the mixture. The vat~~s~~ dyes used earlier in the vatted form showed the same high degree of fastness when applied by spraying in any one of the three forms of "paints". (4) 5 G. casein were beaten up with 100 c.c. of a 5% solution of borax till a clear solution resulted on warming. 5 G. of a suprafix dyestuff (Indanthrene Scarlet GG) were now added to the solution, together with 0.2 g. of hexamethylenetetramine. The paint was well stirred and sprayed on to the cement block to be coloured, and then fixed by steaming in the steaming cottage for 10 minutes. The resulting coloured cement showed some patchiness. It, however, had very ~~g~~good fastness to light (7).

Naphtol dyes whether applied by grinding in the dry state or in the wet state were poor in their fastness to light. These, however, showed the highest fastness to washing. It was moreover observed that by increasing the concentration of the dye the fastness to light could be increased. Azoic dyes derived from the naphthols behave similarly on cotton; the fastness to light of a given azoic combination usually deteriorates with diminishing depth of shade. The quinone-oxime lakes of Naphtol AS, and Naphtol AS-GR had the highest fastness properties both to light and to washing. They also produced bright shades of coloured cements. Substantive dyes showed very poor fastness to light. (1) Metal co-ordinated azo dyes showed improved fastness to light. They, however, did not have the same high degree of fastness as the anthraquinone vat dyes. Attempts to prepare light-fast coloured cements using casein dyed with these colours as the pigments were not successful. Moreover, this type of dyes produced dull shades of coloured cements. The lakes of alizarines gave coloured cements of fastness to light 1 - 4; buthe fastness to washing was also not satisfactory. Anthraquinone vat dyes were used as cement colours in a variety of ways, viz., (1) in the dry state (2) in their vatted form, (3) in the form of their dispersions and emulsions. In the last case they were applied to the cement surface as paints. In all instances these colours were characterised by a very high degree of fastness to light.

The iron oxide colours have excellent fastness properties.

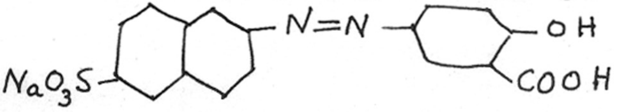
Syntheses of lakes:

Lakes of Chrome Fast Yellow 5G (Ciba) (sodium salt of 6-sulpho-β-naphthalene-azo-salicylic acid).



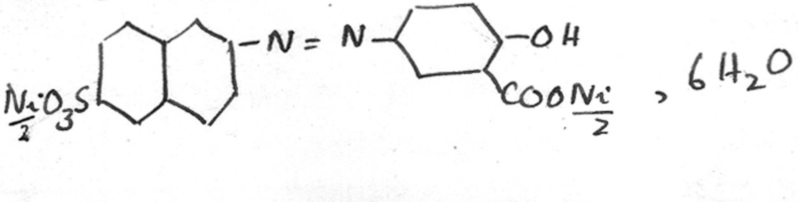
The commercial dye was a yellow powder dissolved in water giving an orange-yellow solution, which became redder on addition of sodium hydroxide (J. Soc. Dyers Col., 1892, 8 75; 1897, 13, 110). It contained sodium sulphate as an adulterant.

The commercial dye (25 g.) was dissolved in the least amount of water. 15 C.c. of moderately concentrated hydrochloric acid (1:1) were added. The bulky yellow precipitate was filtered and washed. The dye was recrystallised thrice from water, giving the half dye acid,



The crystals were golden yellow needles, and on drying at 110°C. gave with N/10 caustic soda theoretical titre with phenolphthalein as indicator. The end point, however, was not easy to perceive. The yield of the pure half dye acid was 44%

<u>Nickel salt of Chrome Fast Yellow 5G:</u> The dye acid (4 g.) was neutralised with Np10 caustic soda, a further 10 c.c. excess of alkali being added. A solution of nickelous nitrate (5 g.) in 50 c.c. of water was added to the dye solution, making up the volume to 500 c.c. Finally the reaction mixture was boiled under reflux for 1 1/2 hours and filtered hot. On cooling, fine golden yellow needles separated. It was filtered off and the precipitate washed until the filtrates ran clear of nickel, and the collected precipitate dried at 105°C. On exposure to the atmosphere, the dried product which assumed an orange colour became golden yellow again. The product, dried at room temperature over calcium chloride, lost <u>8.02%</u> on drying at 100°-105°C. (Calculated for loss of $2H_2O$ from $C_{17}H_{10}N_2O_6SNi, 6H_2O$ = 6.70%). The vacuum dried product lost 19.67% of its weight on drying at 140°-145°C. ($C_{17}H_{20}N_2O_6SNi, 6H_2O$ requires H_2O 20.11%).



The nickel was estimated by first destroying the organic portion by concentrated sulphuric acid, and then precipitating the metal as its dimethylglyoxime lake in the usual way. Sulphur was estimated as barium sulphate, after destroying the organic portion and ~~connecting~~ Converting the sulphur to the sulphate by fusion with sodium peroxide.

The salt dried at 100°-105°C, it gave on analysis the following results: Ni, 11.50%, N, 5.81%, S, 6.33%. $C_{17}H_{10}N_2O_6SNi$, $4H_2O$ requires Ni, 11.6, N, 5.6, S, 6.4%)* Although from an aqueous solution of the nickel salt, nickel was not immediately precipitated in the cold, from the ammoniacal solution it is precipitated by the usual reagents. The nickel salt is very susceptible to the action of mineral acids, which can completely displace the nickel yielding the dye acid, which in one case was isolated and analysed. (Found: N, 7.60. $C_{17}H_{12}N_2O_6S$ requires N, 7.54%).

<u>Attempt to prepare nickel-barium lake</u>: Nickel salt (2 g.) was dissolved in the required amount of hot water, and to this was added 50 c.c. of a 10% solution of barium chloride, when a golden yellow precipitate separated out. The reaction was continued by boiling the mass under reflux for 3 hours. On cooling the precipitate was collected

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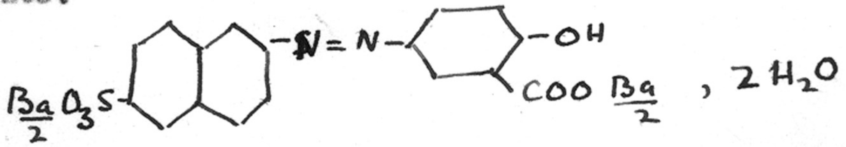
* Footnote: The nitrogen was estimated by the micro-Kjeldahl method and the sulphur by fusion with sodium peroxide and weighing as barium sulphate.

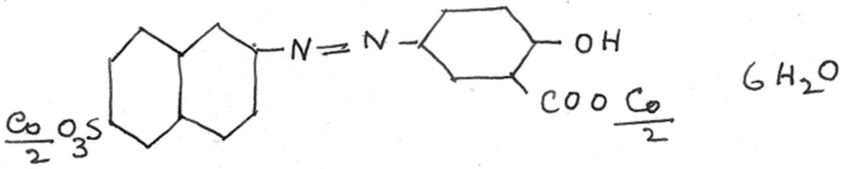
and washed free of nickel, and chloride. It was dried at 100°-105°C. The compound contained only barium and was free of nickel. This dried compound further lost 7.25% of its weight on drying at 135°-140°C. ($C_{17}H_{10}N_2O_6SBa$, $2H_2O$ requires for $2H_2O$ 6.63%). The barium salt dried under vacuum over calcium chloride lost 5.67% of its weight. The barium was estimated as sulphate gravimetrically. (Found: Ba, 24.84, 25.13. $C_{17}H_{10}N_2O_6SBa$, $2H_2O$ requires Ba, 25.23%).

The nickel salt was very sparingly soluble in 95% alcohol, and in pyridine but insoluble in all other solvents. The barium salt was insoluble in pyridine and all organic solvents.



<u>The cobalt salt of Chrome Fast Yellow 5G</u>: The cobalt salt was prepared in an analogous manner to the nickel salt. The cobalt was used in the form of its sulphate. The cobalt was estimated as its sulphate after destroying the organic part of the compound with concentrated sulphuric acid. It was alternatively estimated as its oxide Co_2O_3. Nitrogen was determined by Dumas method. Found for the compound dried

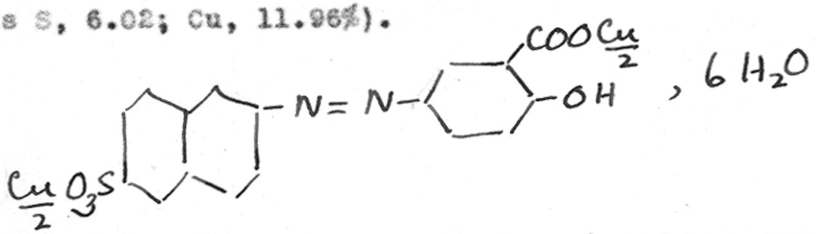
under vacuum over calcium chloride: S, 6.02, 5.88; Co, 10.57, 10.46; N, 5.55. $C_{17}H_{10}N_2O_6SCo$, $6H_2O$ requires S, 6.10; Co 10.91; N, 5.22%). The compound did not lose all the water of crystallisation at 140°C. It lost 17.2% of its weight. $C_{17}H_{10}N_2O_6SCo$, $6H_2O$ requires for $6H_2O$ 20.1%.



<u>Attempt to prepare cobalt-barium lake:</u>

The cobalt salt of the dye was treated with barium chloride solution, similarly to the nickel salt, and the resultant salt dried under vacuum over calcium chloride. The vacuum dried salt lost 7.42% of its weight on further drying at 140°C(± 5°C.). ($C_{17}H_{10}N_2O_6SBa$, $2H_2O$ requires for $2H_2O$ 6.63%). For the vacuum dried product found: Ba, 23.54 ($C_{17}H_{10}N_2O_6SBa,2H_2O$ requires Ba, 25.23%). Found for the product dried at 140°C.: Ba, 25.86. ($C_{17}H_{10}N_2O_6SBa$ requires Ba, 27.62%), whence it is clear that the barium salt was not quite free from the cobalt salt.

Copper salt: The copper salt was prepared similarly to the nickel salt. The product was obtained as yellow needles separating from the filtered solution on cooling. For the vacuum dried product (over phosphorus pentoxide) found: S, 5.71, 5.75; Cu, 11.64. $C_{17}H_{10}N_2O_6SCu$, $6H_2O$ requires S, 6.02; Cu, 11.96%).



Copper lake: The copper reagent employed was cuprammonium sulphate solution, which was prepared by adding excess of ammonia to dissolve completely the precipitate at first formed on adding ammonia to the copper sulphate solution. The half sodium salt of the dye (5 g.) was dissolved in dilute ammonia (200 c.c.), to which was added the cuprammonium sulphate solution containing 7.5 g. of copper sulphate (150 c.c.). The solution was slowly brought to boil, and kept boiling for ~~about~~ 1/2 hour, adding from time to time enough ammonia to ensure the solution ammoniacal. The solution was filtered and kept undisturbed for a week. Fine glistening olive brown plates had separated, which were collected, washed with 250 c.c.

of 10% ammonia solution, and dried under vacuum over calcium chloride in presence of ammonium carbonate. For the vacuum dried lake found: Cu, 17.15, 17.54; S, 5.92; N, 12.53. $(C_{17}H_9N_2O_8\overset{3}{\cancel{N}}S)\frac{3Cu}{2}$, $2H_2O.3NH_3$ requires Cu, 17.27; S, 5.80, N, 12.67%). This lake when dried at 150°-160° lost 9.50% in weight. $(C_{17}H_9N_2O_8\cancel{N}S)\frac{3Cu}{2}$, $2H_2O.3NH_3$ requires for $NH_3.2H_2O$ 9.62%). For the dried product on analysis found: N, 10.38. $(C_{17}H_9N_2O_8\cancel{N}S)\frac{3Cu}{2}$, $2NH_3$ requires N, 11.01%).

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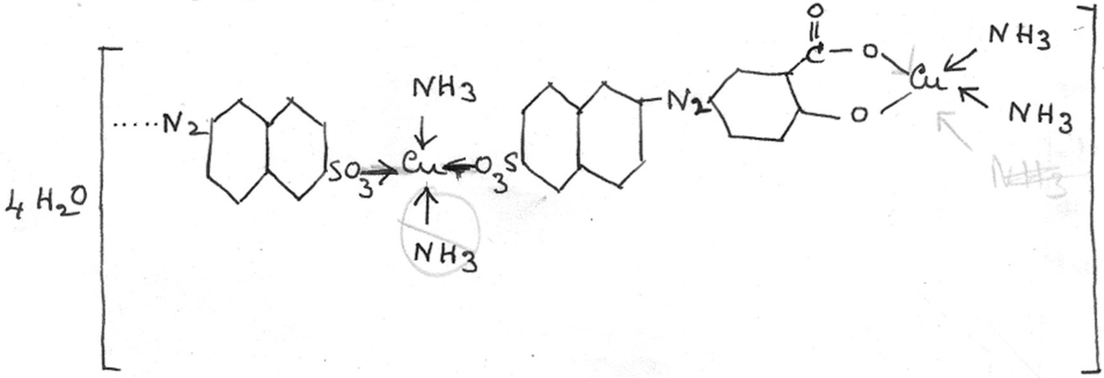
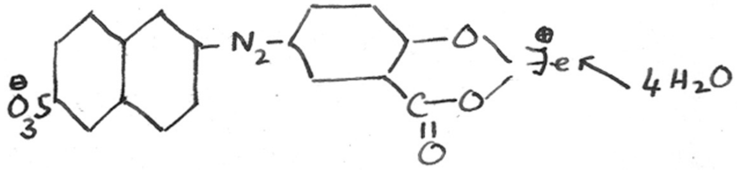
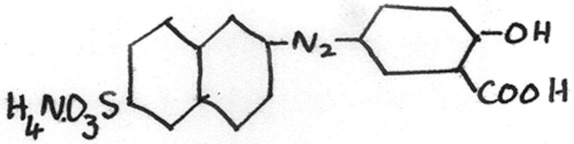
On keeping in air, the product regained 2 mols. of water.



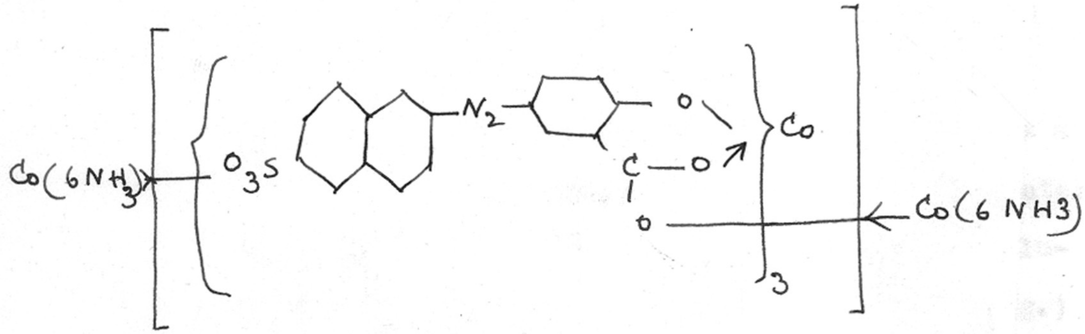
Ferric lake: The half dye acid (2.0 g.) was dissolved in sufficient boiling water to which was added a solution of ferric chloride (1.5 g.). The boiling was continued for 30 mmminutes and then the reaction mixture was allowed to cool. The lake deposited as brownish black plates. It was collected, washed and dried at 100°-105°C. The iron was estimated as its oxide Fe_2O_3. For the vacuum dried lake over calcium chloride found: Fe, 11.24, 11.06. $C_{17}H_9O_6N_2SFe, 4H_2O$ requires Fe, 11.22%. Loss at 150°-160°C. 11.42%. ($C_{17}H_9O_6N_2SFe, 4H_2O$ requires for $3H_2O$ 10.82%).



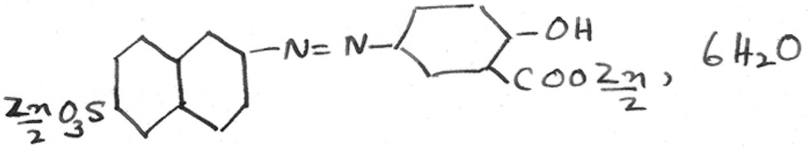
<u>Attempt to prepare ferrous lake</u>: The dye acid (2 g.) prepared by boiling the nickel salt solution containing hydrochloric acid, was dissolved in 200 c.c. of water, to which was added ferrous ammonium sulphate solution (3 g.) containing 15 drops of hydrochloric acid. Immediately on addition of the latter solution, there were deposited fine long brown needles of the iron lake, which decomposed rapidly to give the pure half ammonium salt of the dye. For the half ammonium salt dried at 100°-105°C. found: N, 10.75, 10.60; S, 8.10. $C_{17}H_{15}N_3SO_6$ requires N, 10.80; S, 8.23%).



Cobalt lake: The half dye acid (3 g.) was dissolved in 200 c.c. of water containing 5 c.c. of liquor ammonia. Aquopentammine cobaltic chloride (4 g.) was dissolved in sufficient water containing 10 c.c. of liquor ammonia. The cobaltammine solution was filtered, and poured into the dye solution which was heated to boil, and kept boiling for 15 minutes. At the end of 48 hours, the olive-yellow lake was collected, washed with a dilute solution (10%) ~~s~~of ammonia and water, and the lake was then dried over calcium chloride under vacuum in presence of ammonium carbonate. At the end of a week it was analysed. (Found: Co, 11.37; N, 13.54: $(C_{17}H_8N_2O_6S)_3Co.2(Co(NH_3)_6)$ requires Co, 11.89; N, 13.18).



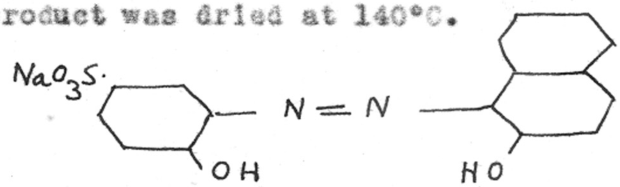
Zinc salt: The dye (2.5 g.) was dissolved in boiling water (250 c.c.). To this added an aqueous solution of zinc chloride (3 g.) slightly made acid (HCl), it gave a solution. It was kept at the boil for 15 minutes. On filtering and allowing to cool, fine yellow needles separated from the solution. The crystals were collected, washed with small quantities of water, and dried under vacuum over sulphuric acid. Zinc was estimated as its oxide after destroying the organic portion of the lake with concentrated sulphuric acid. The beautiful golden yellow product was analysed. (Found: Zn, 11.60, 11.81. Loss at 150°-160°C. 18.69%). $(C_{17}H_{10}O_6N_2S)$ Zn.$6H_2O$ requires Zn, 11.60; $6H_2O$, 19.83%).



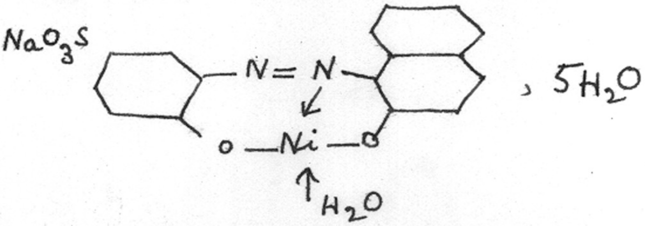
<u>Chrome Fast Violet B (Ciba) C.I. 169</u>. (2'-Hydroxy-4'-sulphophenyl-azo-2-naphthol).

<u>Nickel lake</u>: The commercial sample of the dye was a dark brown powder, giving a bordeaux-red solution in water, a yellowish-red solution in alcohol and deep violet solution in alkalis, and ammonia. The commercial dye (50 g.) was dissolved in 500 c.c. of boiling water and the solution filtered off to free it from gritty matter, which was present in considerable proportion. To the dye solution 25 c.c. of pure hydrochloric acid were added when immediately

a bulky brown precipitate was thrown down. The precipitate was collected and washed with small quantities of water, until Completely ~~more or less~~ free from chlorides and sulphates. The dyestuff yield was 19 g. The product was then repeatedly crystallised from water (thrice) (long brown needles). The product was dried at 140°C.



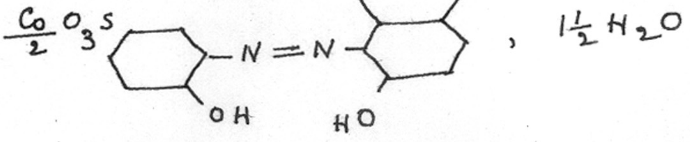
2.66 G. of the crystals were dissolved in 100 c.c. of water containing 3 c.c. of liquor ammonia. The solution was slowly brought to boil, and 2.5 g. of nickel nitrate dissolved in 25 c.c. of water were added to the boiling dye solution, when a bulky crystalline (long needles) precipitated of the nickel lake was thrown down. The reaction mixture was kept boiling for a prolonged period of 2 hours. On cooling the precipitate was collected, and washed and dried under vacuum over phosphorus pentoxide. For the vacuum dried product found: S, 5.82; Ni, 10.62, 10.15; N, 5.33. Loss at 150°C. 20.20%. $C_{16}H_9N_2SO_5NiNa,6H_2O$ requires S, 6.02; Ni, 10.35; N, 5.26; $6H_2O$, 20.34.



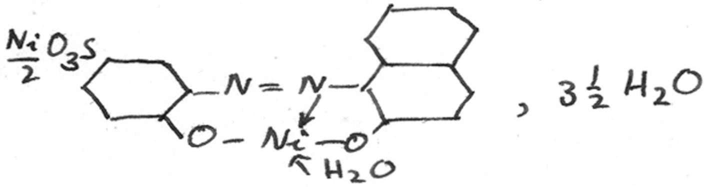
2 G. of the product were extracted (Soxhlet) with 98% alcohol until about 1 g. was extracted. The extract and residue were dried at 130°C. and analysed. For the residue found: S, 7.21; for the extract S, 7.50. $C_{16}H_9N_2SO_6NiNa$ requires S, 7.55.

The product was soluble in ammonia and alkalis giving a deep violet solution. It also gave a deep violet solution with concentrated sulphuric acid. With alcohol it gave a red solution, and with pyridine a violet solution. It was insoluble in all common organic solvents.

<u>Cobalt salt of Chrome Fast Violet B</u>: The sodium salt of the dye (2 g.) were dissolved in 50 c.c. of water containing 3 c.c. of liquor ammonia. The filtered solution was boiled to expel ammonia. 3 G. of an aqueous solution of cobalt nitrate were added to the dye solution, and the mixture brought to boil, and refluxed for ~~about~~ 1 hour. On filtering and cooling minute red plates of the cobalt simple salt separated, which were collected, washed and dried at 100°-105°C. Found: Co, 7.39, 7.00; loss at 160°C. C, 5.83. $(C_{16}H_{11}N_2O_5S)_2Co$, 1 1/2$H_2O$ requires Co, 7.40; 1 1/2 H_2O, 6.78.

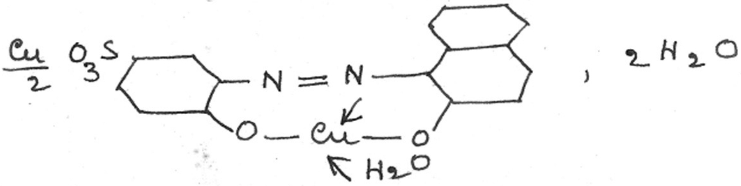


<u>Di-nickel lake</u>: The purified sodium salt (2 g.) was dissolved in water, and to the boiling dye solution was added a solution of nickel chloride (4 g.). After keeping the solution at the boil for about 15 minutes, a bulky precipitate of a fine crop of needles separated. The supernatant solution was only slightly coloured. The lake was collected and thoroughly washed with water. It was dried at 100°-105°C. For the dried lake found: Ni, 17.23; loss at 160°C. 15.86%. $C_{16}H_9N_2SO_5\frac{3Ni}{2}$, 4 1/2 H_2O requires Ni, 17.26; 4 1/2 H_2O, 15.69%.



<u>Attempt to prepare Nickel-barium lake:</u> To 1 g. of the sodium salt of the dye, dissolved in sufficient boiling water was added an aqueous solution of nickel chloride (1.5 g.) followed by 25 c.c. of 10% barium chloride solution. The reaction mass was refluxed for an hour, ~~from~~ on cooling the fine needle~~s~~ shaped crystals were collected and washed free from chloride. The lake was free from barium and was identical with the former nickel lake.

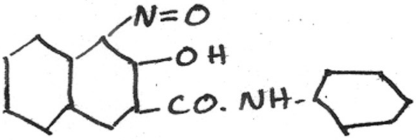
Copper lake: The sodium salt of the dye (2 g.) were dissolved in sufficient boiling water and 3 g. of copper sulphate dissolved in sufficient water added, and the mass kept boiling for half an hour, when fine feathery chocolate brown needles separated. The product was dried at 100°-105°C. For the dried product found: Cu, 19.23, 19.09. Loss at 160°C. 6.83%. $(C_{16}H_9N_2O_5S)\frac{3Cu}{2}$, $3H_2O$ requires Cu, 19.30; $2H_2O$, 7.35%.



Lakes of nitroso derivative of Naphtol AS.

Preparation of the nitroso derivative of Naphtol AS: Naphtol AS (1/100 mol.) (2.65 g.) was dissolved in 100 c.c. of water containing 0.5 g. of caustic soda and 1.4 g. of sodium nitrite in 100 c.c. of water added. To the mechanically stirred mixture (1:3) dilute sulphuric acid was added until reaction was acid to Congo Red. Reaction was completed by slowly bringing the mixture to boil and keeping it boiling for 10 minutes. Nitrous fumes were evolved. A bright orange precipitate separated, which was collected, washed and dried at 100°-105°C. The yield was 2.7 g. This substance was not very pure but could be crystallised from xylene or acetic acid (m.p. 202°C.). (*Vide* Battegay, Ch. Langjahr and P. Reting, *Chemie et. industrie*, 1924, **11**, 453; Goldstein and Stenton, *Helv. Chim. Acta*, 1938, **21**, 56; Stenhouse and Groves, *Ann.*, 1877, **189**, 153; Groves, *J. Chem. Soc.*, 1884, **45**, 292; Liebermann and Jacobson, *Ann.*, 1882, **211**, 48; Russig, *J. prakt. Chem.*, (2) 1900, **62**, 56; Zincke, *Ann.*, 1900, **278**, 188; Graudmogin and Michel, *Ber.*, 1892, **25**, 981; Smith and Taylor, *J. Am. Chem. Soc.*, 1935, **57**, 2460; Fuchs, *Ber.*, 1875, **8**, 1026; Lagodzinski and Hardine, *Ber.*, 1894, **27**, 3076; Henriques and Ilinski, *Ber.*, 1885, **18**, 705; Kochler; *D. R. P.* 25,469).

Alternative method of preparation of the nitroso derivative of Naphtol AS: 1.32 G. of the purified Naphtol AS (m.p. 242°C.) were dissolved in 250 c.c. of boiling 98% alcohol. 0.69 G. of sodium nitrite (twice theoretical) was dissolved in 10 c.c. of water, and 5 c.c. of glacial acetic acid were added, then refluxed on the water bath for 1/2 an hour, and allowed to cool on the water bath. After 48 hours, the solution was cooled in ice and the crystalline bright orange-red plates were collected and washed with a small quantity of alcohol and with boiling water, the product was dried. Yield 0.45 g. of the very pure product. This compound melted and decomposed at 202°C. Found: N, 9.73%. $C_{17}H_{12}N_2O_3$ requires N, 9.59%.



0.5 G. of the nitroso derivative similarly prepared was dissolved in 30 c.c. of alcohol and 0.2 g. of caustic soda. 0.5 g. of aniline hydrochloride was diazotised in the usual manner, but the diazo solution was not found to couple with the nitroso derivative, which was recovered unchanged. For the nitroso derivative found: N, 9.93. $C_{17}H_{12}N_2O_3$ requires N, 9.59%).

Attempt at preparation of lakes of The nitroso derivative of Nephtol AS ~~derivatives~~:

1. Cobalt lake: Nephtol AS (5.4 g.) was dissolved in a small quantity of water containing 3 g. of caustic soda and the solution made up to 500 c.c. To this solution were added 2.0 g. of sodium nitrite and the mass ~~were~~ was cooled (5°C.) and stirred mechanically. To the mixture were added 6 g. of cobalt sulphate dissolved in 100 c.c. of water and containing the required amount of hydrochloric acid to render the whole acid to Congo Red. At the end of 3 hours the mass was heated until it boiled vigorously and

gave off nitrous fumes. The reddish brown precipitate was then collected, washed and dried, but was found to contain only a trace of cobalt.

Nickel and iron similarly did not yield any pure lakes, although nickel gave an impure nickel compound.

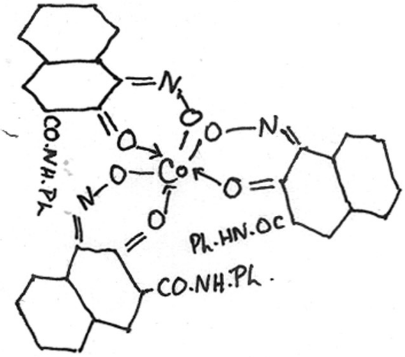
2. <u>Cobalt lake:</u> The nitroso derivative (6 g.) was refluxed with (250 c.c. of 98% alcohol for an hour, when only a fraction of the compound went into solution. To the solution 50 c.c. of an alcoholic solution of cobalt nitrate (10 g.) were added. The mass was refluxed for 8 hours. At the end of 8 hours the substance was collected and washed with small amounts of alcohol and then with water. The product (3.7 g.) dried at 100°-110°C. was very sparingly soluble in alcohol (98%), soluble in xylene, less so in toluene and benzene, but readily soluble in boiling pyridine. This product was extracted with alcohol (98%), and the residue (1.2 g.) analysed. Found: Co, 4.23, 4.35. $(C_{17}H_{11}O_3N_2)_2Co$ requires Co, 6.31%.

3. <u>Nickel lake:</u> Naphtol AS (5.4 g.) was dissolved in a small quantity of water containing 2 g. of caustic soda, and the diluted solution to 500 c.c. by addition of dilute caustic soda solution. To this was added 2xg.sodium nitrite (2 g.). Glacial acetic acid (10 c.c.) and nickel nitrate

(6 g.) in 100 c.c. were added to the clear solution, and the mixture was slowly warmed and brought to boil, when a further 25 c.c. of acetic acid were added. After keeping the mixture at the boil for 30 minutes, it was cooled and the deep purple precipitate collected and washed. Yield 5.6 g. The crude product was extracted with benzene. A dirty brown substance not containing nickel (0.7 g.) was removed. The residue was further extracted with 98% alcohol to remove any unreacted Naphtol AS. For the final residue (2 g.) found: Ni, 7.80. $(C_{17}H_{11}O_3N_2)_2Ni$ requires Ni, 9.14%. The product was evidently still not very pure.

Preparation of the lakes of the nitroso derivative of Naphtol AS:

Cobalt lake: The purified Naphtol AS (m.p. 242°-43°C.) (2.62 g.) was dissolved in 300 c.c. of boiling 98% alcohol. To the clear solution was added an aqueous solution (100 c.c.) of 0.937 g. of cobalt sulphate and 3.0 g. of sodium nitrite. 10 C.c. of glacial acetic acid were immediately poured in, and the mass refluxed for 2 hours. At the end of that period 10 c.c. of concentrated hydrochloric acid were added. The bright maroon-red precipitate (powder) was collected and washed with water and a small quantity of alcohol (50 c.c. of 95%). Yield of dry product (100°-110°C.) 2.6 g. Found: Co, 6.24, 6.32. $(C_{17}H_{11}O_3N_2)_3Co$ requires Co, 6.31%; $(C_{17}H_{11}O_3N_2)_2Co$ requires Co, 8.79%. Hence the compound is the former one.

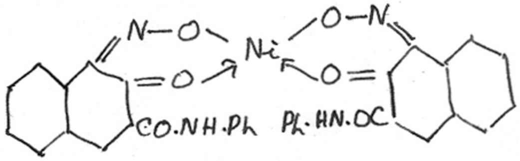


The preparation was repeated by taking twice the amount of cobalt sulphate, and the reaction mixture was refluxed for 6 ~~houss~~ hours instead of for 2 hours. The bright maroon precipitate gave on analysis Co, 6.47, 6.42; N, 9.15. $(C_{17}H_{11}O_3N_2)_3Co$ requires Co, 6.31; N, 9.01%.

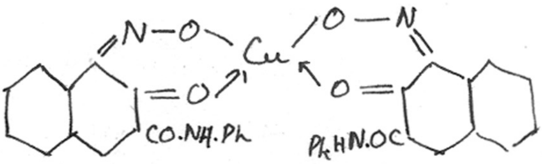
The lake was insoluble in boiling alcohol, very sparingly soluble in acetone, and also in the usual solorganic solvents (e.g. solvent naphtha, benzene, chlorobenzene, etc.). It was readily soluble in pyridine giving a deep red solution. It was likewise soluble in chloroform. It dissolved in boiling nitrobenzene to give a deep red solution. With concentrated sulphuric acid it gave a red solution, giving a yellow precipitate on dilution. It was unaffected by ammonia and caustic alkalis. As the lake was not easily crystallisable from any solvent a small quantity of the lake (1.0g.) was dissolved in sufficient boiling chloroform and to the filtered clear solution added 50 c.c. of boiling petroleum ether (50°-70°C.) when a slight turbidity appeared, an amorphous powder being deposited on keeping. For the bright maroon powder found: Co, 6.03, 6.25. $(C_{17}H_{11}O_3N_2)_3Co$ requires Co, 6.31%.

<u>Nickel lake:</u> Naphtol AS (2.62 g.) in 300 c.c. of 98% boiling alcohol was nitrosated and condensed with nickel by adding nickel nitrate and 3.0 of sodium nitrite followed by 10 c.c. of glacial acetic acid and boiling the mass under reflux for 6 hours. Further 10 c.c. of glacial acetic acid were added at the end of 6 hours. The lake was separated by filtering hot and was washed successively with water (500 c.c.), alcohol (50 c.c.) and a small quantity of

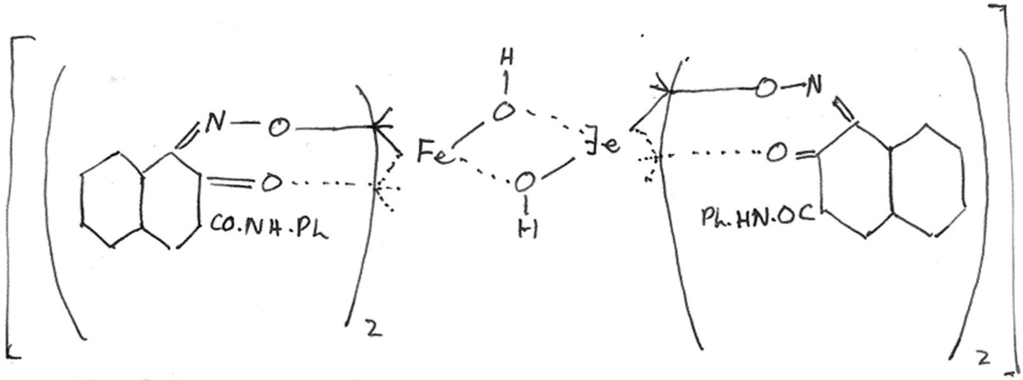
acetone. The lake (2.1 g.) was dried at 100°-110°C. For the lake dried at 100°-110°C. found: Ni, 9.25, 8.97; N, 9.06. $(C_{17}H_{11}O_3N_2)_2Ni$ requires Ni, 9.14; N, 8.74%. $(C_{17}H_{11}O_3N_2)_4Ni_3$ requires Ni, 13.16%. The lake is the former compound. The nickel lake was sparingly soluble in acetone, very little soluble in alcohol. It, however, went into solution readily in boiling pyridine giving a deep purple brown solution. In concentrated sulphuric acid it dissolved to give a purple solution. The lake could by hydrolysed by prolonged boiling with concentrated hydrochloric acid, and the nitroso compound could be recovered.



<u>Copper lake:</u> The lake was prepared as before by taking the Naphtol AS and copper $(Cu(CH_3COO)_2.2H_2O)$ in the molecular proportion of 2:1. The Naphtol AS (2.62 g.) gave 2.3 g. of the lake (dried at 100°-110°C.). The production analysis gave Cu, 9.70, 9.82; N, 8.56, 8.74. $(C_{17}H_{11}O_3N_2)_2Cu$ requires Cu, 9.97, N, 8.66%. $(C_{17}H_{11}O_3N_2)_4Cu_3$ requires Cu, 14.12%. The compound is the former one.



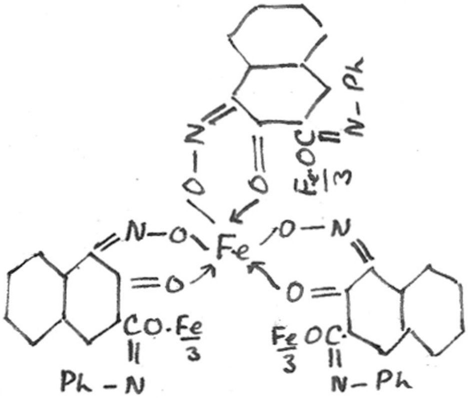
Lake with ferrous iron: Naphtol AS (2.62 g.) dissolved in 300 c.c. of boiling alcohol was refluxed with 1.97 (1/2 atom Fe) of ferrous ammonium sulphate in 50 c.c. of water containing 10 c.c. of glacial acetic acid and an aqueous solution of sodium nitrite (3 g.). After refluxing for half an hour, the intense green lake, which had separated in fine crystalline plates was allowed to stand for two hours. It was then collected, and washed with boiling water (500 c.c.) and then with alcohol until the washings were slightly green. It was ~~then~~ washed with a small amount of ether and dried at 100°-110°C. The dried product was a fine glistening, intensely green, fluffy crystalline mass. Yield 2.4 g. Found: Fe, 9.29, 9.20. $(C_{17}H_{11}O_3N_2)_2Fe(OH)$ requires Fe, 8.53%. In another preparation with 1 atomic proportion of iron for 1 mol. of the Naphtol found for the product: Fe, 8.91, 8.74. N, 8.76. $(C_{17}H_{11}O_3N_2)_2Fe(OH)$ requires Fe, 8.53; N, 8.55%.



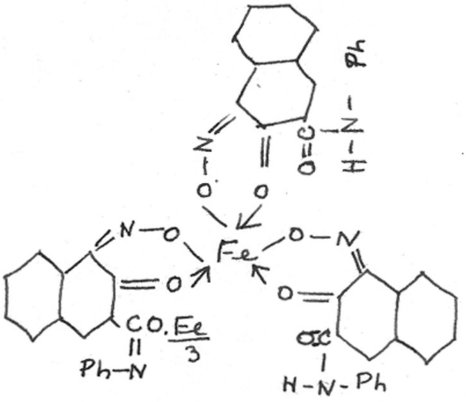
The lake (0.5 g.) was boiled with concentrated hydrochloric acid in a conical flask fitted with a Bunsen valve. After boiling for about 10 minutes, the flask was cooled under a tap. The lake had decomposed to yield the nitroso compound and ferric chloride. The usual analytical tests failed to give indication of the presence of ferrous iron in the lake, the iron was entirely present in its tervalent state.

Ferric lake:(I). The Naphtol AS (2.62 g.) of the was dissolved in boiling alcohol and 3 g. of sodium nitrite dissolved in a small quantity of water (10 c.c.) added followed respectively by an alcoholic solution of ferric chloride containing 3 g. of the dihydrate, and 10 c.c. of glacial acetic acid. The reaction was carried out on a boiling water bath for one hour, at the end of which 25 c.c. of dilute sulphuric acid (containing 2 c.c. of concentrated acid) were added. The fine crystalline plates of the deep green lake were collected and washed with

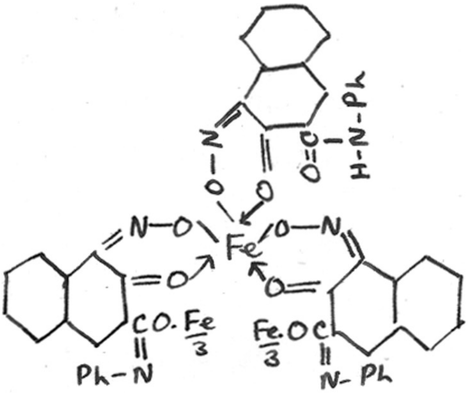
500 c.c. of boiling water, and then with small quantities of alcohol until the filtrates were distinctly green. The lake was dried at 100°-105°C. For the lake found: Fe, 11.38, 11.36; N, 8.40. $(C_{17}H_{10}O_3N_2)_3Fe_2$ requires Fe, 11.40; N, 8.49%.



Ferric lake (II): The lake was prepared exactly like the previous one, but one third atomic proportion of iron was taken for 1 mol. of the Naphtol AS. The precipitate was collected and washed with 500 c.c. of boiling water and small quantities of alcohol until the filtrates ran green. For the lake dried at 100°-110°C. found: Fe, 7.94, 8.06; N, 8.40. $(C_{17}H_{14}O_3N_2)_3\frac{4Fe}{3}$ requires Fe, 7.88; N, 8.87%. It was seen that even if only one third atomic proportion of iron was taken for 1 mol. of the Naphtol the simple lake $(C_{17}H_{11}O_3N_2)_3Fe$ was not formed, but instead $(C_{17}H_{11}O_3N_2)_3\,\frac{4Fe}{3}$.

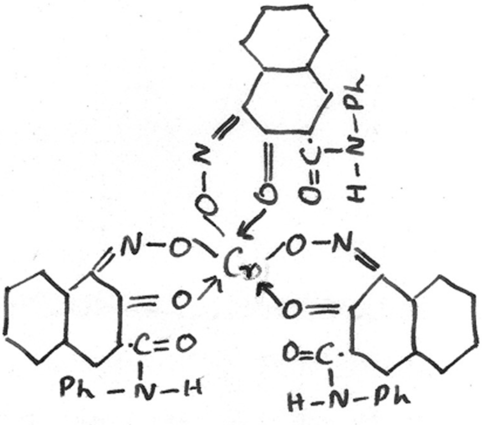


<u>Ferric lake (III):</u> The Naphtol AS (2.62 g.) in presence of nitrous acid was condensed with iron taken in the form of ferric <u>alum</u> (2.67 g.) solution in acidulated water (containing 1 c.c. concentrated sulphuric acid). The precipitate, which was a lively green became deeper on further refluxing. At the end of 1 hour the reaction was complete. For the lake dried at 100°-110°C. found: Fe, 10.00, 9.96; N, 8.81. $(C_{17}H_{11}O_3N_2)_3\,\frac{5Fe}{3}$ requires Fe, 9.93; N, 8.70%.



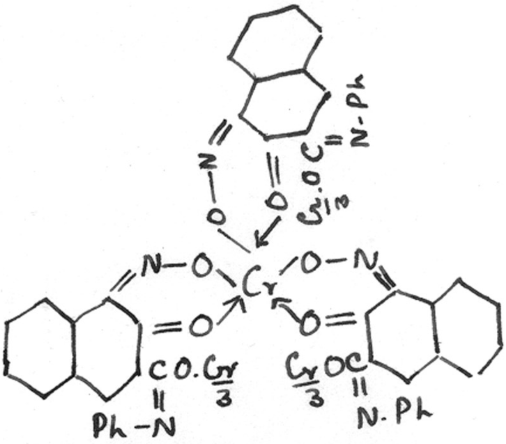
<u>Chromium lake (I)</u>: The lake was prepared in the usual manner, but the reaction was completed by finally adding 10 c.c. of concentrated hydrochloric acid and further refluxing for 30 minutes, when a clear brownish red solution resulted, from which on filtering and keeping no solids separated at the end of 36 hours. Addition of 100 c.c. of water, however, produced a turbidity, and at the end of 48 hours a bright brown precipitate had separated which was collected and washed, first with a very small quantity of alcohol, and next with 500 c.c. of warm water. The lake (0.9 g.) was dried and analysed. For the lake dried at 100°-110°C. found: Cr, 6.12, 6.62; N, 8.39. $(C_{17}H_{11}O_3N_2)_3Cr$ requires Cr, 5.56; N, 9.09%. The chromium lake was prepared as before, but instead of

adding hydrochloric acid at the end, acetic acid was added and refluxed when the reddish precipitate first formed slowly went into solution. The filtered solution was poured into 1 litre of distilled water when a reddish brown precipitate separated which was carefully washed successively with small quantities of boiling water, alcohol and ether. For the dried product on analysis found: Cr, 6.20; N, 8.40. $(C_{17}H_{11}O_3N_2)_3Cr$ requires Cr, 5.56; N, 9.09%.



<u>Chromium lake (II):</u> The preparation was repeated with excess (more than 1 atomic proportion of chromium for one mol. of the Naphtol AS) of chromium chloride. The lake was precipitated by pouring the clear solution into a large volume of water. Found Cr, 10.43, 10.17. $(C_{17}H_{11}O_3N_2)_3Cr_2$ requires Cr, 10.64%. Found in another preparation Cr, 11.13

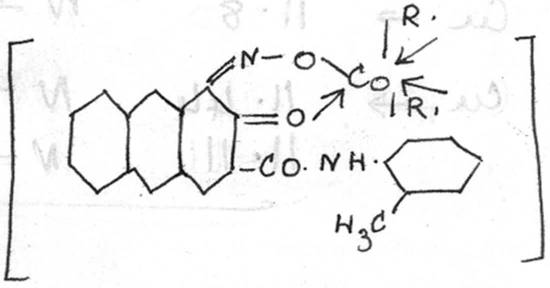
$(C_{17}H_{11}O_3N_2)_3Cr_2$ requires Cr, 10.64%.



Nitroso derivative of Naphtol AS-GR: The Naphtol AS-GR was purified as usual. The nitroso derivative was obtained as in the case of Naphtol AS from an alcoholic solution or from a solution in acetone. For the nitroso derivative prepared from acetone found: N, 7.62. For the product prepared from alcohol found: N, 6.84. $C_{22}H_{16}N_2O_3$ requires N, 7.87%. The products so prepared did not melt below 340°C.

Lakes of nitroso derivative of Naphtol AS-GR:

Cobalt lake: Naphtol AS-GR (1.63 g.) was dissolved in 250 c.c. of boiling alcohol to which were added concentrated aqueous solutions of cobalt sulphate (0.94 g.) and sodium nitrite (1 g.). To the reaction mass were added 10 c.c. of glacial acetic acid when an intense purpe colouration developed. It was refluxed for 1 hour, and then 5 c.c. of concentrated hydrochloric acid ~~was~~ were added and it was further refluxed for 2 hours and allowed to stand overnight. It was filtered washing the lake successively with boiling water, alcohol and acetone in which the lake was soluble, giving a purple solution. The lake was a dull purple. For the air-dried product found: Co, 5.02, 5.45; N, 7.32. $(C_{22}H_{16}N_2O_3)_3Co$ requires Co, 5.24; N, 7.45%.



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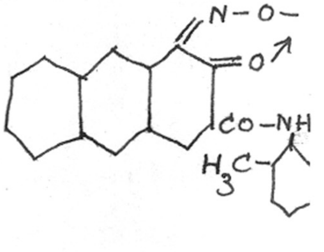
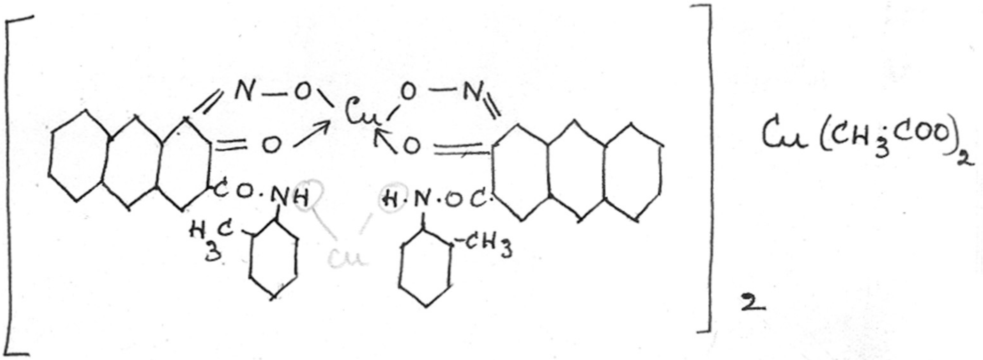


Copper lake: The Naphtol AS-GR (1/2 mol.) (1.63 g.) was hetreated with 0.50 g. of copper acetate (1/4 atom) in presence of 1 g. of sodium nitrite and 20 c.c. of acetic acid. The resultant bright reddish-brown lake was dried at 100°-110°C. and analysed. Found: Cu, 11.11; N, 6.48. $[(C_{22}H_{16}N_2O_3)_2Cu]_2Cu(CH_3COO)_2$ requires Cu, 11.65; N, 6.84%. The preparation was repeated, taking for 1 mol. of Naphtol AS-GR, 1 atom of Cu. Found for the lake Cu, 11.44; N, 6.92%.



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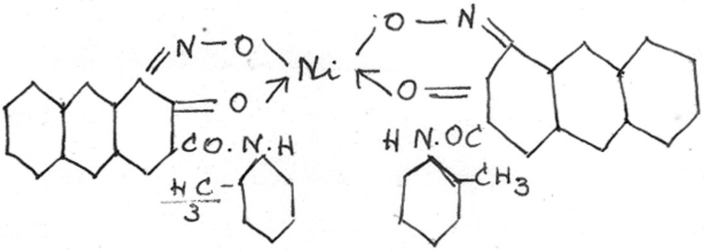
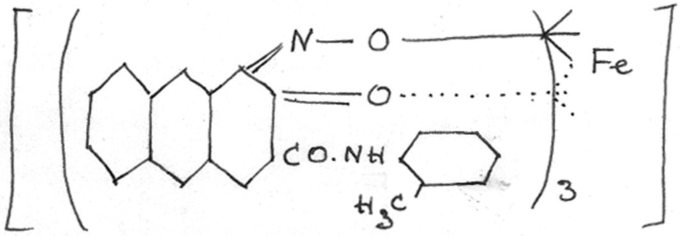
Nickel lake: Naphtol AS-GR (1.090 g.) ~~d~~was condensed with 0.397 g. of nickel chloride (alcoholic solution) in presence of sodium (1.0 g.) nitrite and acetic acid (10 c.c.) For the deep maroon lake on analysis found: Ni, 7.85, 7.72: $(C_{22}H_{16}N_2O_3)_2Ni$ requires ~~Ne~~Ni, 7.63%.

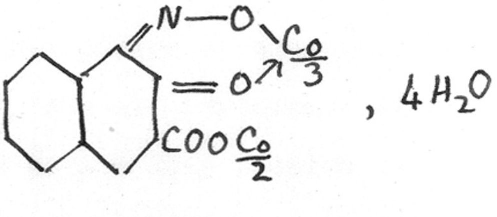


<u>Iron lake</u>: Naphtol AS-GR (1.090 g.) was condensed with iron 0.653 g. of ferrous ammonium sulphate solution containing 2 c.c. of concentrated sulphuric acid ~~and~~ in presence of 5 c.c. of acetic acid and 1 g. of sodium nitrite. As the reaction was very sluggish, it was continued for 8 hours. For the air dried compound found: Fe, 5.03; N, 7.61. $(C_{22}H_{15}N_2O_3)_3Fe$ requires Fe, 4.87; N, 7.48%. The iron was wholly present in its trivalent form.



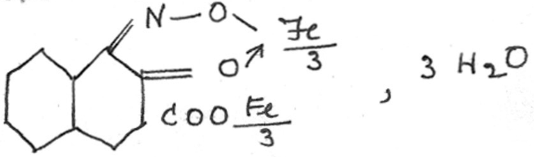
Lakes of the nitroso derivative of 2-hydroxy-3-naphthoic acid:

Cobaltous cobaltic lake: The 2-hydroxy-3-naphthoic acid (m.p. 217°C.) (3 g.) was dissolved in 200 c.c. of boiling 98% alcohol. A solution of sodium nitrite (3 g.) in 20 c.c. of water was added, followed by cobalt nitrate (6 g.) in 50 c.c. of a mixture of 40 c.c. of alcohol and 10 c.c. of acetic acid. It was refluxed for 5 hours, and 10 c.c. of concentrated hydrochloric acid were added and further refluxed for 1 hour. At the end of the period the minute ~~x~~crystalline plates (reddish brown) were collected and washed with boiling water (1 litre). The washings were a light orange colour. The lake was then washed with a small quantity of alcohol (orange washings) and dried at 100°-110°C. when it became a deep purple. The product retained 4 mols. of water. For the substance found: Co, 14.78 14.43; N, 4.13. Loss at 130°C., 8.54. $C_{11}H_5O_4N.\frac{5Co}{6}$, $4H_2O$ requires Co, 14.63; N, 4.16; 1 1/2H_2O, 8.10%.



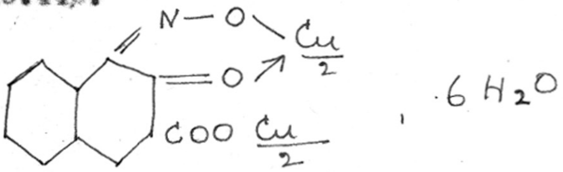
The lake gave a reddish brown solution with concentrated sulphuric acid, which became straw yellow on dilution. It was very sparingly soluble in boiling water (pale yellow). In ammonia and dilute caustic soda it gave a reddish orange solution (dissolving completely). It was insoluble in benzene, alcohol and acetone, but completely dissolved in pyridine giving a reddish brown solution.

Di-ferri lake: The lake was prepared in a similar manner to the cobaltous cobaltic lake. The ferri salt employed was the ferric chloride. The olive-black minute plates of the lake were collected and washed and dried as before. On drying the lake became dark brown. On analysis found: Fe, 12.82; N, 3.70. $C_{17}H_8O_4N.\frac{2Fe}{3},3H_2O$ requires Fe, 12.20; N, 4.57%.

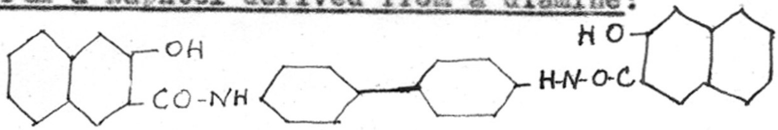


The lake was insoluble in water and all common organic solvents (benzene, solvent naphtha, chlorobenzene, acetylene tetrachloride, chloroform, alcohol and acetone). It dissolved in ammonia giving a deep green solution, and also in dilute caustic soda and pyridine. With concentrated sulphuric acid it gave a deep reddish brown colouration, on dilution gave a straw yellow solution.

~~The~~ Di-cupri lake: The lake was prepared exactly as in the previous two cases. The cupri salt chosen was the chloride. Found for the lake: Cu, 16.44, 16.56, 16.97. $C_{11}H_4O_4N,6H_2O$ requires Cu, 16.44%.

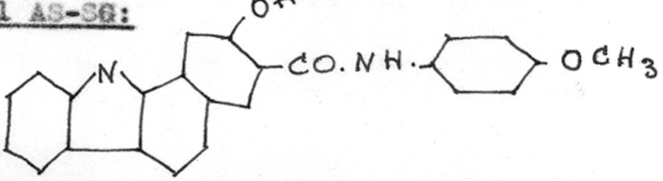


Attempt to prepare the nitroso derivative and its lakes from a Naphtol derived from a diamine:



The nitroso derivative was not formed. Found for the pure Naphtol N, 5.05. $C_{34}H_{24}O_6N_2$ requires N, 5.32%. The Naphtol had altered its colour to pale maroon on treating with nitrous acid in alcoholic solution. Found for the dried product: N, 5.50. $C_{34}H_{24}O_6N_2$ requires N, 5.32%. The cobalt lake was not ~~isolated.~~ formed

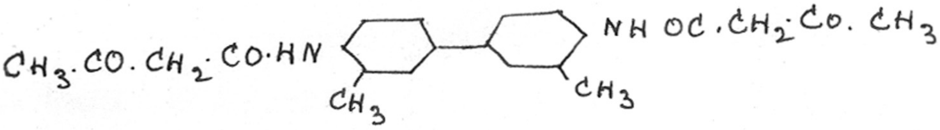
Attempt to prepare the nitroso derivative of Naphtol AS-SG:



The Naphtol purified as usual by washing away the soluble impurities and then precipitating the Naphtol from a filtered solution of caustic soda by means of carbon dioxide was crystallised from nitrobenzene (greenish yellow needles). The action of nitrous acid did not produce the nitroso compound when tried in the usual manner. Found for the product N, 7.27. The Naphtol $C_{24}H_{17}O_3N_2$,Mirequires N, 7.37%.

Attempt to prepare lakes of diketones:

Naphtol AS-G:

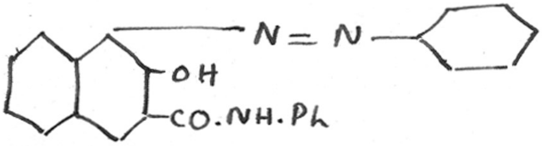


The Naphtol AS-G (1.5 g.) (softening at 199°C. and decomposing at 204°C.) was dissolved completely in 200 c.c. of 98% alcohol. 3 G. of nickel chloride dissolved in alcohol were added to the solution of the Naphtol AS-G and refluxed for 6 hours. The mass was allowed to cool. The precipitate which had separated on cooling was collected, washed with water and alcohol and dried at 100°-110°C. Found for the dried product Ni, traces; N, 7.63. The Naphtol AS-G requires N, 7.37%.

Attempt to prepare the iron lake of Naphtol AS-G:

The pure Naphtol AS-G (3 g.) was dissolved in 350 c.c. of boiling absolute alcohol to which was added an alcoholic solution of ferric chloride. There was an immediate change of colour of the reacting solution. It gave a light purple colouration. On refluxing for 4 hours, the mass was filtered. On cooling a purple solid had deposited, which was collected and dried. It was next dissolved in chloroform and filtered off (0.8 g.). The filtrate brought to dryness and digested with water, the resultant gummy product was impure and contained ~~indifferent~~ indefinite amounts of iron.

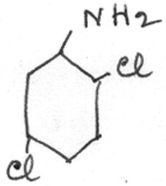
Attempt to prepare lakes of the dye derived from Naphtol AS and diazo benzene:



The dye was crystallised from nitrobenzene (m.p.238°C.) from solvent naphtha (m.p. 236°C.). The dye (2 g.) was partly suspended and dissolved in 300 c.c. of alcohol. 3 G. of nickel chloride dissolved in alcohol ~~was~~ were added and refluxed for 48 hours, at the end of which the dye was recovered unchanged (softening at 232°C. melting at 235°C.). Found: Ni, traces only.

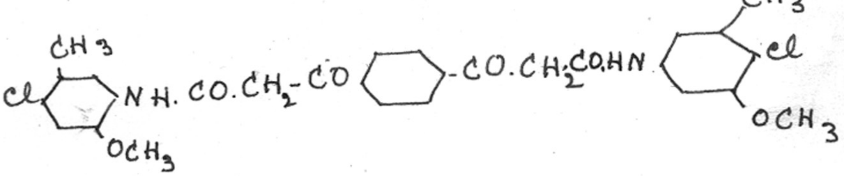
Copper lake was also not formed under similar conditions. 2 G. of the dye ~~was~~were dissolved in 350 c.c. of glacial acetic acid to which were added a solution of 20g. of cupric acetate in glacial acetic acid and refluxed for 8 hours, at the end of which the dye was recovered unchanged.

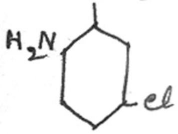
Attempt to prepare copper and chromium lakes of the dye from Naphtol AS-G and Fast Scarlet Salt GG:



The dye obtained from commercial Naphtol AS-G and Fast Scarlet Salt GG was thoroughly washed with water. 2.5 G. of the finely ground dye were refluxed with 250 c.c. of water for 1 hour, and to the ~~mixture~~ suspension was added a solution 2.5 g. of chromium acetate. The mass was refluxed for 5 hours, at the end of which, it was filtered and the orange yellow dye was carefully washed with boiling water. It was found to be free from chromium.

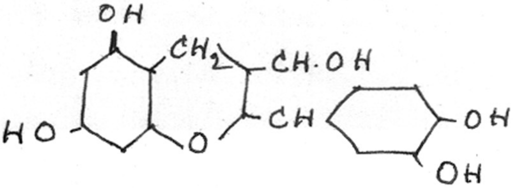
A similar experiment was conducted to see if the copper lake was formed, with negative result. Coupling of the diazo salt in presence of the metal salts also did not give the lakes. The dye from Naphtol AS-LG and diazotised Fast Red Base TR also did not form a lake with copper or chromium.





Attempt to prepare the iron derivative of Naphtol AS: Pure Naphtol AS (2.62 g.) was dissolved in 250 c.c. of boiling absolute alcohol to which was added an alcoholic solution of 3 g. of ferric chloride, when a deep purple colouration developed. It was refluxed for 3 hours and the boiling solution filtered off. Fine hexagonal plates were deposited from the filtrate on cooling, which, on washing with water, resinified. The dried gummy product gave on analysis Fe, 2.61, 1.86%, which does not conform to any compound.

Catechin (acetyl derivative):

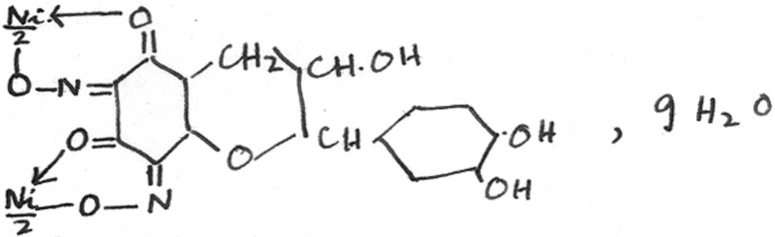


The substance (m.p. 195°-196°C.) (2 g.) was taken in a round bottomed flask to which were added 10 c.c. of acetic anhydride and 10 drops of dry pyridine and fefluxed for 3 hours. The contents of the flask were then poured into ice-cold water and the product that separated (2 g.) was collected and crystallised from alcohol (fine needles). It melted at 164°C.

Dinitroso derivative: Catechin (1 g.) was dissolved in 150 c.c. of water and 1 g. of pure sodium nitrite added and the mass refluxed. Fifteen minutes later, 5 c.c. of glacial acetic acid were added to the solution and then refluxed for 1 hour, when the solution had profoundly altered in colour (from pale straw to deep reddish brown). However, the nitroso derivative could not be isolated.

Nickel lake of the dinitroso derivative of catechin: Catechin (2.90 g.) was dissolved in 150 c.c. of boiling water. Sodium nitrite (2.80 g.) in 25 c.c. of water was added followed by 2.91 g. of nickel nitrate and 10 c.c. of glacial acetic acid. It was boiled under reflux for 2 hours. The brown lake was washed with a small quantity of boiling water and 500 c.c. of cold water and dried at 100°-105°C. Found: Ni, 10.40, 10.29; N, 4.85. $C_{15}H_{12}N_2O_8Ni,9H_2O$ requires

Ni, 10.33; N, 4.93%.



Synthesis of iron oxide pigments.

Reduction of nitrobenzene to aniline: Nitrobenzene (100 g.), water (60 c.c.) and 35% hydrochloric acid (12 c.c.) were taken in a 500 c.c. 3-necked round bottomed Pyrex flask. The mass was agitated by means of a mechanical stirrer, passing through the bulb condenser. A thermometer to note the temperature of the reaction mass was introduced through one neck. The mass was heated up to 100°C. and the flame removed. Through the other side neck the iron filings were slowly added, 1 g. at a time. In the first few minutes there was hardly any reaction, taking place. However, gradually the reaction built up and the liquid mass began to boil. Addition of too large a quantity of iron resulted in undue frothing. Before adding a further quantity of iron care was taken to see that the iron already added had been completely acted upon. The addition of 120 g. of the iron filings occupied nearly 3 hours, the liquid refluxing all the time. The reaction was complete at the end of 5 hours, when the mass was transferred to another long narrow necked round bottomed flask, and the mass made slightly alkaline by addition of a few drops of 20% caustic soda. The mass was then steam-distilled. The oil that distilled over was pale yellow at first, but became browner gradually. The yield of aniline was 80-85% in the various experiments. The oxide sludge was 165 g. and was a black, and very soft pigment.

25 G. each of this aniline sludge were fired in a gas fired muffle at 400°, 600°, 800°, ~~and 900°~~ and 1000°C. respectively. The sludge was taken in a large silica dish and spread out in a thin layer. It was kept in the muffle for 1 hour at the respective temperatures. It was observed that in the beginning the change in the shade of the pigment was very rapid, it attained a certain permanent shade at any particular temperature after about an hour, and this shade could not be further changed merely by keeping the mass for a prolonged period at the same temperature. If the temperature were altered, however, there was a distinct change of shade. The iron oxide fired at 400°C. was a yellowish brown pigment containing 97.1% ferric oxide, that fired at 600°C. was a red pigment containing 97.8%.

ferric oxide, that fired at 800°C. a maroon pigment containing 98.1% ferric oxide, and finally the pigment obtained by firing the sludge at 1000°C. was a maroon pigment containing 98.6% ferric oxide. The black oxide contained iron oxide in the ferrous state also. But apparently it was unaffected by atmospheric conditions. The shades of the oxides became deeper the higher the temperature of ignition, e.g. at 600°C., the oxide was a red, while at 1000°C., it was a deep maroon. The lower the temperature of ignition, the softer was the pigment, while at higher temperatures it decidedly became gritty, and was difficultly reacted upon by potassium bisulphate.

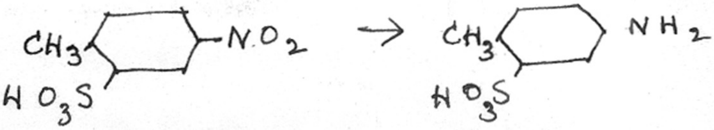
<u>The analysis of the oxides:</u> The black was the only oxide which contained iron in the ferrous state also. A weighed amount of it was digested with 10 c.c. of hydrochloric acid (pure 35% acid) in a small conical flask fitted with a Bunsen valve, and kept on a boiling water bath. When the sludge had completely gone into solution, the solution was made up to a known volume and aliquot portions titrated with standard potassium dichromate solution, using orthophenanthraline ferrous complex as indicator. The black oxide contained FeO, 13.1% and Fe_2O_3, 84.6%. The total iron oxide was estimated as follows. About 0.5 g.

of the iron oxide, ground well in a glass or agate mortar, was accurately weighed out and taken in a 30 c.c. Pyrex test tube, and 3.5 g. of pure potassium bisulphate were then added to the test tube, which was well shaken. The test tube was clamped and heated gently until the potassium bisulphate melted and then gradually increased the temperature until a clear amber coloured solution resulted. The mass was allowed to cool, and on cooling the cake came off on treating with cold water. The mass dissolved easily in dilute hydrochloric acid. The solution was made up to desired volume and the iron oxide was estimated by titrating aliquot portions of the solution.

The estimation did not prove easy. An aliquot portion of the solution was reduced by stannous chloride solution and the excess stannous chloride was oxidised by a solution of mercuric chloride. The resultant ferrous solution did not give a satisfactory end point with potassium dichromate using a solution of diphenylamine in concentrated sulphuric acid as indicator, nor were the results encouraging when orthophenanthroline ferrous complex was used as the indicator. This complex indicator itself seemed to react with the tin or mercury salts. Xylene

Cyanol FF was employed as an alternative indicator, but it did not improve matters. Finally standard ceric sulphate solution was used as the oxidant. With this reagent, although orthophenanthroline ferrous complex yielded poor results Xylene Cyanol FF gave excellent results. With the 0.015N ceric sulphate solution employed 1/2 drop of the reagent towards the end point, changed the colour of the solution from yellowish green to pink. The end point was very sharp. The colour of the solution towards the end point persisted sufficiently long (at least 10 minutes), and then slowly changed back to yellowish green.

Reduction of p-nitrotoluene-2-sulphonic acid: The p-aminotoluene-2-sulphonic acid was obtained from the nitro compound by reducing the nitro compound by metallic iron.



The compound (110 g.) was dissolved in 60 c.c. of water and 100 c.c. of a dilute solution of hydrochloric acid, containing 8.5 c.c. of (35% hydrochloric acid) were added and the mass mechanically agitated in a 3-necked round bottomed Pyrex flask. The mass was brought to 100°-105°C.

Iron filings (B.D.H.) (84 g.) were added to the mass, a little at a time. The reaction proceeded smoothly, and there was no frothing or foaming taking place at any instant if the temperature was not allowed to rise above 105°C. In about 1 1/2 hours all the iron filings were added and the mass refluxed further for 2 hours. At the end of thatths period the mass was filtered hot and the black sludge repeatedly broken up and digested with boiling water to ensure maximum recovery of the amine. The washings and filtrates were concentrated to a small bulk, and if necessary a few c.c. of concentrated hydrochloric acid added. Yield of the amino compound (85 g.) 91%. Yield of sludge 100 g..

The sludge was ignited at various temperatures, e.g. 400°, 600°, 800° and 1000°C. respectively. The oxide obtained in the first instance was red, the second slightly bluer in tone, while the third and fourth were definitely maroonsr. The black oxide contained FeO, 6.6%; Fe_2O_3, 72.3%. The oxide ignited at 400°C. gave Fe_2O_3, 97.6%, at 600°C. 97.4%, at 800°C. 97.5%, and at 1000°C. 97.7%.

The effect of addition of aluminium, zinc, nickel and copper in the form of metal or salt on the pigment:

Aluminium: The reduction was carried out as before, but instead of taking 84 g. of iron filings, 80 g. of iron filings and 8 g. of aluminium dust were added. Yield of the amino compound 70 g. The sludge was lighter in colour than without aluminium, but the pigments were all steel grey of very slightly varying shades. The black oxide contained Feo, 19.67%, but Fe_2O_3 only 58.6%. The oxide fired at 400°C. contained Fe_2O_3 79.7%, while that ignited at 600°C. 83.7%.

Zinc: Zinc dust (8 g.) was substituted for aluminium dust. The sludge was quite black and the oxides ignited at 400°C. and 600°C. and 800°C. were respectively brownish red, brownish maroon and maroon. Yield of amino compound a.70 g. Fe_2O_3 in pigments fired at 400°C. 81.4%; at 600°C. 82.1% and at 800°C. 83.6%. Black oxide, 76.9%.

Nickel: Nickel nitrate (20 g.) wa~~s~~ added to the nitro compound. There was no appreciable difference in the colour of the ~~d~~reduction sludge. Yield of the amino compound 73 g. The oxide obtained by igniting the sludge at 800°C. contained Fe_2O_3,89.1%.

Copper: Copper sulphate (20 g.) was added to the solution of the nitro compound and the reduction carried out as usual. The sludge was substantially similar in nature to the one with iron only. Yield of amino compound 72 g.

<u>Reduction in presence of sodium chloride</u>: The nitro compound was reduced without addition of any hydrochloric acid. Instead, however, an equivalent quantity of sodium chloride was taken. The reduction went to completion. The yield of the amino product and the nature of the "sludge" of iron oxide were exactly similar. Yield of amino compound 72 g. The sludge fired at 800°C. contained Fe_2O_3 98.6% and was of a similar shade to the pigment obtained by igniting the sludge obtained by reducing the nitro compound by iron in presence of hydrochloric acid.

<u>Cement water-proofing agents:</u>

<u>"Impermo" Cement water-proofing compound</u> (Cement Marketing Co., England): A white, light, finely divided powder reacting strongly alkaline to phonolphthalein, litmus and Linstead's mixed indicator. Calcium was present in large quantity. The compound contained a considerable proportion of free lime, which was present as slaked lime. The compound was submitted to a quantitative inorganic analysis as follows:

About 0.5 g. of the substance was accurately weighed and digested with concentrated hydrochloric acid (5-10 c.c.). On cooling the mass was diluted to 100 c.c. and a small quantity of a fatty material which had caked on the surface was separated by filtration, on a filter paper of know ash. The filter paper was left in a desiccator for 48 hours at the end of which it was incinerated and strongly ignited to give "insolubles" (silica)". From the filtrate aluminium and iron were separated as their hydroxides and estimated as oxides, and calcium was estimated by titration of the oxalate against standard permanganate solution. Magnessium and "SO_3" were estimated as usual. The loss on ignition was determined by strongly igniting the substance in a gas fired muffle (1100°C.) and the moisture was estimated by distilling it in presence of an entrainer.

The fatty material which separated on treating with hydrochloric acid was qualitatively tested and was found not to contain nitrogen, sulphur and the halogens. It went in solution in a dilute sodium bicarbonate solution and gave a titre with caustic soda using phenolphthalein as indicator. It was therefore an acid. It did not decolourise an aqueous permanganate solution, bromine water also was not decolourised. It burnt completaly, leaving no residue. It was insoluble in water either in the cold or boiling. It melted at about 60°C. The percentage of fatty matter was determined by taking 10 g. of the water-proofing compound and treating it with 50 c.c. of concentrated hydrochloric acid in 150 c.c. of water, and refluxing the mixture after the first reaction with evolution of large quantity of heat had subsided, for about an hour. The mass was left undisturbed overnight, and ether extracted. The ether extract was weighed in a small beaker. The extract was pale brown. The ether extract was dried and dissolved in boiling alcohol and was refluxed with addition of charcoal, and crystallised out of alcohol. The resulting crystals were pure white and had a fatty odour.

The compound gave CaO, 64.38, Al_2O_3 + Fe_2O_3, 1.45; "SO_3", 0.79; Moisture, 1.7. Total loss on ignition, 32.26%. Percentage of fatty acid, 13.0%.

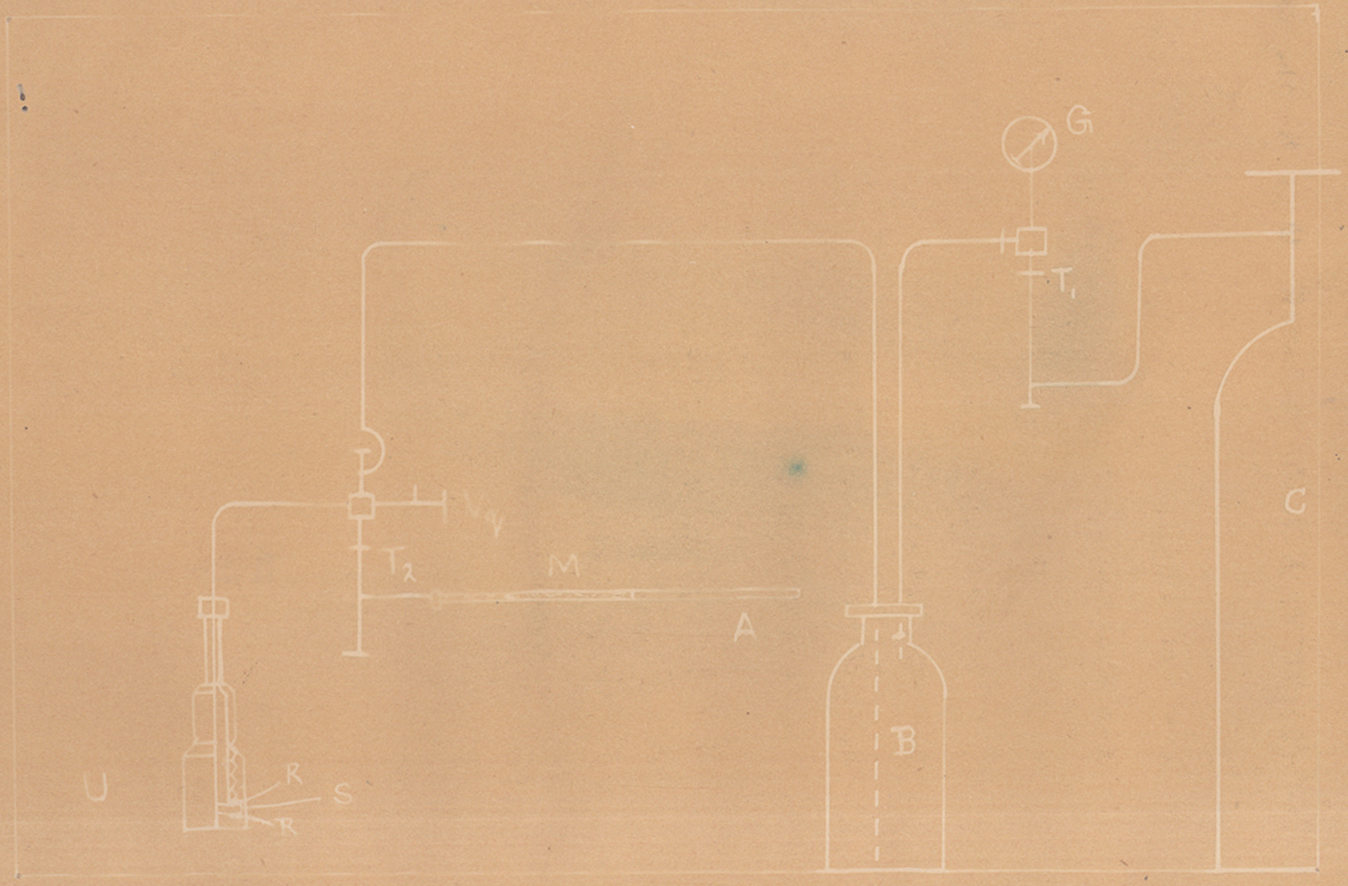
The m.p. of the ~~noice~~ thrice crystallised fatty acid was 65°-66°C. (palmitic 62°C., stearic 69°C.). m.p. of lead salt 112°C. Mixed m.p. of lead salt 109°-110°C..

Moleculer weight by alkali titration 317 (stearic acid 284). Molecular weight of the acid by silver salt method 285. Therefore the fatty acid in "Ompermo" is a commercial stearic acid.

"Pudlo" water-proofing compound: This was also a light, pure white, finely divided powder reacting strongly alkaline to phenolphthalein. When acidified with fairly concentrated hydrochloric acid (1:1), it yielded a fatty material which floated on the surface. Found for the compound Silica, 0.31%, Al_2O_3 + Fe_2O_3, 0.14%; $Ca(OH)_2$, 78.68; MgO traces; fatty acids, 22%; loss on ignition 37.16%.

The fatty material was qualitatively tested and gave negative results for nitrogen, sulphur and halogens. It was soluble in sodium bicarbonate solution, was not affected by aqueous permanganate solution or by bromine water, and was insoluble in cold or boiling water. The fatty matter was therefore a fatty acid. It was crystallised from alcohol (charcoal) twice and gave snow white crystals melting indefinitely 56-63°C. M.p. of lead salt 110°-111°C. Mixed m.p. of lead salt of a pure specimen of stearic acid and the lead salt 107°C. Mean mol. weight by alkali titration 296. Mean mol. weight by silver salt method 291. Hence the fatty matter was a commercial stearic acid.

High pressure permeability apparatus: The apparatus is self explanatory. It consists of a brass cup ending in


G
T₁
VV
T₂
M
A
B
C
U
R
S
R

An apparatus for the determination of permeability:

A - Air bubble
B - Pressure bottle
C - Compressed air cylinder
G - Pressure gauge
M - Manometer
R - Rubber washers
S - Cement sample
T_1)
)- High pressure valves
T_2)
U - Brass union
V_q - Quick release valve

a union which holds the cement sample between rubber washers. The cement sample itself is prepared in the form of a disc, 1 1/2" in diameter and 3/16" thick. To the cup is secured a copper capillary with a high press valve block which connects it respectively to the pressure bottle, quick release valve and the manometer. The manometer is a stout glass capillary sealed at one end and connected to the high press valve by means of a glass-metal joint. A small length of the glass tube is filled with air, and this air column advances or recedes on the scale and is calibrated to indicate variations in pressure within the system when the valve T was closed. The pressure bottle is of mild steel and can easily withstand pressures upto 14 atmospheres that were employed for testing purposes.

<u>Working</u>: The thin circular (3/16" thick) cement test piece ~~could~~ prepared under specific conditions is kept in the union. The quick release valve is connected to a vacuum pump and the union exhausted. The quick release valve is closed and the air cylinder valve opened and the water released under press into the union. Now the press of the water is noted (gauge reading). The union is disconnected from the pressure bottle by means of the high pressure valve. The air column advances steadily and affords a very sensitive

instrument for the measurement of water percolating through the test piece. The permeability of water will be proportional to the manometer reading. The volume of water forced through the test piece will be proportional to the drop in pressure and the manometer reading.

The volume of water forced through the test piece will reduce the total volume of water in the system, and consequently will reduce the pressure. V, the total volume of water is directly proportional to the pressure. When the volume decreases the pressure proportionately falls. The manometer reading increases inversely:

$V \propto P \propto \frac{1}{L}$ or $V = \frac{K}{L}$ where K is a constant. When some water has percolated through the test piece, the manometer reading will have increased to say L_1. Then

$$V = \frac{K}{L}, \quad V_1 = \frac{K}{L_1} \quad \text{whence} \quad \frac{V}{V_1} = \frac{L_1}{L}.$$

Both L and L_1 are know and V the original volume is a constant which can be measured. Hence the volume of water percolated can be known. The temperature and humidity can be both found and controlled.

There is, however, an additional aspect of the problem which has to be carefully noted. All test pieces have only one surface in contact with water, the other similar surface being away from it. Both these surfaces will offer a greater resistance to the passage of water than the main body of the test piece. This is partially due to the fact that these surfaces are in contact with the atmosphere and the free lime on the surface is neutralised by carbon dioxide of the atmosphere and hence a more impermeable membrane of cement will be formed on the exterior. In addition, however, carefully we might prepare the test-pieces, a small per cent of the smaller particles of cement will find their way out and fill up the surface voids better than the voids in the interior. The surface will show a "skin effect" and errors due to this can be eliminated by carefully grinding away a thin section off the surfaces.

No readings on the apparatus could be taken for lack of time.

Regarding the information required according to O. 215K Handbook, University of Bombay), I beg to state that the sources from which information has been derived and references to the literature of the subject, on which the present work is based, have been mentioned in the introductory part of the thesis. General guidance has been received from Dr. K. Venkataraman, D.Sc.(Manc.), F.I.C., A.M.I.Chem.E., Mody Professor of Chemical Technology and Head of the Department of Chemical Technology, The University, Bombay. I take this opportunity of expressing my deep sense of gratitude to him for his inspiring guidance throughout. I am also grateful to Dr. G. P. Kane for the help given to me in connection with "Waterproof cements".

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University Teacher

Candidate