AZO AND AZOIC DYES BASED ON NATURALLY OCCURRING RAW MATERIALS

A Thesis
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to the

UNIVERSITY OF BOMBAY

for the degree
of
Ph. D.

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Part I

Further experiments on naphthols with paraffin chains.

INTRODUCTION

Since the introduction of Naphtol AS (the anilide of β-hydroxynaphthoic acid) by the Griesheim Elektron in 1911, a number of Naphtols have been synthesised capable of giving a variety of shades in combination with diazo salts and differing widely in fastness properties. The Naphtols, possessing many advantages, such as ease of application, brightness and cheapness, found a ready market in this country. The production of a Naphtol or azoic dyeing, depends on the dual function of impregnation in a secondary phenolic component in the form of its sodium salt and developing in the solution of a primary component, or diazotised amine, marketed as Fast Colour Base or its soluble form, the diazo salt. While the method itself appears simple, to get a really good dyeing possessing satisfactory fastness to light, washing and rubbing, proper choice of the Naphtol, the base and after-treatment are essential requisites. In view of the importance of the Naphtols to the textile industry, synthetical experiments were undertaken in this laboratory as part of a general study on the chemistry and tinctorial properties of the Naphtols (cf. Forster, Mehta and Venkataraman, J. Soc. Dyers Col., 1938, 54, 209; Forster, Ramachandran and Venkataraman, ibid., 216; Mehta and Thosar, ibid., 1940, 56, 160; Bhat, Forster and Venkataraman, ibid., 166). While the azoic colours are known to possess good fastness properties towards light and washing, their main weakness in a large number of cases has been their inferior fastness to rubbing. The importance of the rubbing factor would be realised by the fact that this dyed yarn constitutes the coloured border for dhoties, sarees and is also used in shirtings, i.e. types of fabrics where excellent fastness to rubbing is a desideratum.

In the course of investigations on insoluble azo dyes, both in substance and on the fibre, Rowe and his collaborators (J. Soc. Dyers Col., 1929, 45, 67; ibid., 1921, 37, 204; 1924, 40, 218; 228, 230; 1925, 41, 278, 354; 1926, 42, 82, 207), Ruperti (Melliand Textilber., 1927, *8*, 942) and Schol (*ibid*., 1928, *9*, 1002) carried out pioneering work on the effect of after-treatments on shade and fastness of azoic dyeings. After-treatment with hot alkaline solutions for an appropriate period increased the fastness to light and rubbing.

The improvement effected in fastness properties by the soaping after-treatment is well known. Some dyeings, which are initially fugitive to light and washing and loose to rubbing, have been known to acquire good all round fastness. In general, the fastness to rubbing bears a direct relationship to the soaping after-treatment, although any unduly prolonged treatment might affect adversely the fastness to light.

Apart from factors such as efficient pre-treatment of the material, thorough hydroextraction and addition of protective colloids to the developing bath, which are well understood as leading to dyeing of good fastness, especially to rubbing, two factors clearly play a dominant role in determining the rubbing fastness of an azoic dyeing. One is the substantivity of the Naphthol, since it is the azoic dye derived from that portion of the Naphthol not substantively adsorbed, but mechanically retained by the yarn, is responsible for the rubbing off effect. The second factor is the efficient removal of this azoic dye by the soaping after-treatment.

Cohoe and Cohoe (*Ind. Eng. Chem., Anal. Ed.*, 1932, *4*, 112) have defined substantivity as the attraction between a dye in solution and a fibre it colours. Although the precise meaning of substantivity and the relation between this factor in a Naphthol and the fastness properties of the azoic dyeings are still obscure, substantivity would appear to be a useful feature, especially in package dyeing and with regard to the reduction of the conditions of after-treatment. According to Rowe (*J. Soc. Dyers Col.*, 1931, *47*, 29) the substantivity is a characteristic property of the naphthol depending on its chemical constitution. It would, however, appear that the fastness properties of the naphthol dyeings is a specific property of the azoic dye and cannot be attributed to either of its components. Certain specific groupings in the Naphthol or the base, however, are known to exercise their influence in modifying the fastness (Forster *et al*, *loc. cit.*). The phenomenon of substantivity, at least as far as cotton is concerned, can only be attributed to adsorption and the play of secondary or residual valencies, although in the case of protein fibres chemical combination may be attributed. Ruggli (J. Soc. Dyers Col., Jubilee Volume, 1934, 77) reviewed the structural features that are favourable to substantivity. Enumerated, they are (a) a symmetrical structure; (b) the presence of the acid amide group (-CO-NH-) as evidenced by the much greater substantivity of Naphtol AS over β-naphthol; (c) unsaturation; (d) the sulphur atom and (e) heterocyclic rings.

In the course of a study of rubbing fastness properties of azoic dyes, the present author attempted (M.Sc. Thesis, Madras University, 1940) to take both these factors (substantivity and after-treatment) simultaneously into account by synthesising naphthols with constitution so modified that on the one hand substantivity could be obtained and on the other, the reagents (such as soap and other detergents) employed in the after-treatment exercised a certain solvent or emulsifying action towards the azoic dye precipitated on the fibre. Naphthols were synthesised using fatty acids of the type of lauric, myristic, palmitic, and unsaturated acids of the type of cinnamic and oleic, since these, containing as they do, a hydrophilic hydroxyl and hydrophobic paraffin chain, were expected to confer on the resulting product a bi-polar character leading to colloidal solution. Colloidal nature being an adjunct of a substantive molecule (cf. Rath, *J. Soc. Dyers Col.*, 1923, *39*, 334), it was anticipated that the naphthols would be highly substantive, giving dyeings having a high degree of fastness. The naphthols synthesised were all characterised by excellent fastness to rubbing, while fastness to kier-boiling and light exhibited certain variations. Wide differences were noticeable in the depth of shades between those derived from the saturated fatty acids and that from oleic acid, the latter giving a weak shade. In view of the observation of Ruggli (*loc. cit.*) as to the advantages of unsaturation, this seemed inexplicable although a possible explanation lies in the fact of the substitution of the aliphatic chain having taken place in the *meta* position in the arylamide half of the naphthol component.

Try ~~[illegible]~~ aminoacyl oleic acids

Difficulties were encountered in effecting dissolution of the naphthols prepared from the saturated fatty acids and additions, such as pine oil, had to be made to solubilise them ~~and~~ even in as moderate concentrations as 1% on volume, showing thereby its inadaptability for large scale use in the industry. As between the N-2-hydroxy-3-naphthoyl-N'-lauryl-p-phenylenediamine and its stearyl counter part, it was noticed that the former was comparatively more easy to dissolve, although even in this case pine oil could not be dispersed with, leading to the presumption that synthesis effected with fatty acids of lower molecular weight would render dissolution easy preserving at the same time the admittedly beneficial effects conferred by the introduction of the~~s~~ aliphatic radicle.

Hartley ("Wetting and Detergency", p. 153; J. Chem. Soc., 1938, 1768) demonstrated the solvent action of soaps and synthetic detergents containing long paraffin chains on organic substances sparingly soluble in water. Hartley pictures such solubility as being due to the paraffin chain ions collecting in large aggregates or micelles in which the grease, oil or other organic substances form liquid solutions. Although it may have no bearing on detergency, Hartley's work on the solvent action of soaps and detergents has great significance with regard to the after-treatment of azoic dyeings with soaps or synthetic detergent solutions (Rowe, et al, J. Soc. Dyers Col., 1921, 37, 204; et sequa).

Since improvement in the fastness to rubbing of an azoic pigment involves the removal of the superficially precipitated pigment, and since soap, the common detergent used, has solvent action on organic compounds, the introduction of a long paraffin chain was considered of special interest from the point of view of the production of azoic dyes with increased solubility in soap solutions, and therefore, with increased rubbing fastness. If the aliphatic residue is introduced by acylating a mono-2-hydroxy-3-naphthoyl-p-arylenediamine, the resulting naphthol will have an increased substantivity by virtue of the carboxylamide group. Such naphthols are of greater interest in view of the abundance of aliphatic acids in this country and the resultant cheapness of the final product.

In view of these considerations it was thought desirable to use in the synthesis fatty acids again, Try α-β- unsatg acids

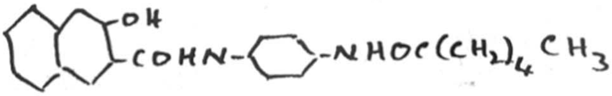
~~Naphthenic~~

Aliphatic

Aromatic

but having lower molecular weight such as caproic, caprylic and capric. Since unsaturation should normally lead, according to Ruggli (loc. cit.), to naphthols of high substantivity having good tinctorial power, ~~and~~ syntheses have been effected using acids of the type of oleic, mixed linseed oil fatty acids and naphthenic acids. Since these acids are known to confer good wetting power (especially the last named) when suitably used, it was anticipated that these naphthols will have good penetrating power and as such should prove level dyeing. Other factors favourable to substantivity such as the presence of a heterocyclic structure and methoxyl, have also been taken into account to effect the synthesis of a few new naphthols

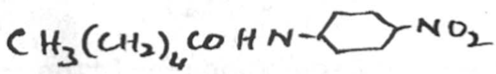
- Naphthol (I)



has now been synthesised by condensing mono-N-caproyl-p-phenylenediamine (X) q with paper

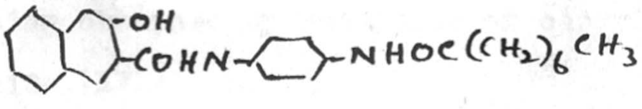
(X)

prepared by the reduction of caproyl-*p*-nitranilide (XIV)



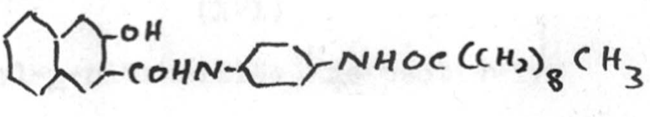
with β-hydroxynaphthoic acid chloride. Using caprylic and capric acids as above, N-2-hydroxy-3-naphthoyl-N'-caprylyl-*p*-phenylenediamine (II)

Propo?



(II)

and N-2-hydroxy-3-naphthoyl-N'-capryl-*p*-phenylenediamine (III)



(III)

have been prepared by condensing 2-hydroxy-3-naphthoyl chloride with mono-N-caprylyl-*p*-phenylenediamine (XI)

(XI)

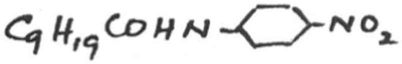
and mono-N-capryl-*p*-phenylenediamine (XII)

(XII)

these being obtained by reduction of caprylyl-*p*-nitranilide (XVI)

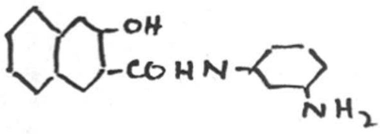
(XVI)

and capryl-*p*-nitranilide, respectively.



(XVII)

With the same object in view, i.e. of introducing a long paraffin chain, tetrahydroanacardic acid, the hydrogenated product of anacardic acid (pentadecadienyl salicylic acid) (cf. Ruheman and Skinner, *J. Chem. Soc.*, 1887, T663; Smit, *Proc. K. Akad. Wetenshappen*, Amsterdam, 1931, **34**, 165; Pillay, *J. Ind. Chem. Soc.*, 1935, **12**, 226) has been condensed with mono-2-hydroxy-3-naphthoyl-m-phenylenediamine (XIII)



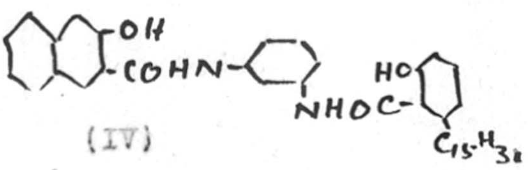
(XIII)

to produce naphthol (IV)

Sample?

?

p!



(IV)

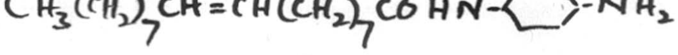
Give the condn process?

In view of the o-hydroxycarboxylic acid structure and in addition to the long paraffin chain, it was expected that this naphthol would have increased substantivity and good rubbing fastness. It has since been found that, though possessing advantages of easy dissolution and brightness of shade, the shades obtained were weak; the fastness to rubbing was, however, very good. Naphthol~~s~~ (V) has now been synthesised

Why?

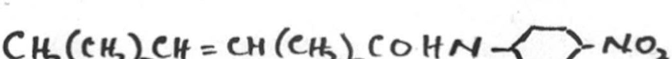
(V)

by condensing mono-N-oleyl-p-phenylenediamine (XIV)



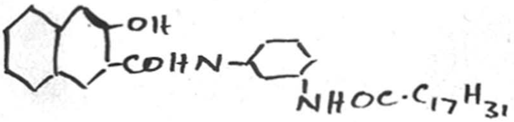
(XIV)

obtained by the reduction of oleyl-p-nitranilide (XVIII)

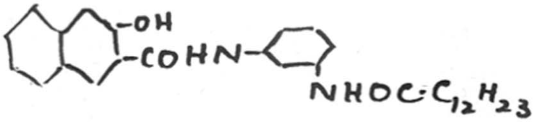


(XVIII)

with β-hydroxynaphthoyl chloride, while naphthols (VI) and (VII) were prepared by condensing linseedyl



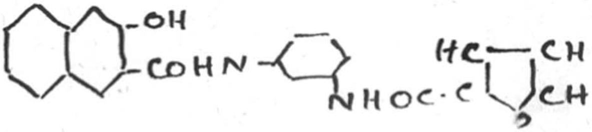
(VI)



(VII)

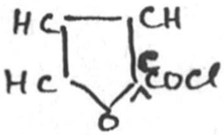
and naphthenyl chlorides with mono-N-2-hydroxy-3-naphthoyl-*m*-phenylenediamine.~~respectively~~. All these naphthols presented no difficulties during dissolution and had good rubbing fastness. The shades obtained, however, especially in the case of naphthols (VI) and (VII) were weak. In view of the fact that nephthols (IV), (VI) and (VII) where the substitution of aliphatic chain had taken place in the *meta* position in the arylamide half of the naphthol component gave uniformly weak shades, having poor light fastness, while possessing good fastness to rubbing, experimental work Mostall? is being carried out to prepare the *p*-isomers. The explanation for this striking phenomenon probably lies in the fact that these exert a stereochemical influence on the ability of the molecule to be absorbed by cellulose. It may also be due, as explained by Robinson and Mills 2 (*Proc. Roy. Soc.*, 1931, 131, 576, 596) to the complexes of the *meta* dyes being too large.

Naphthol (VIII)



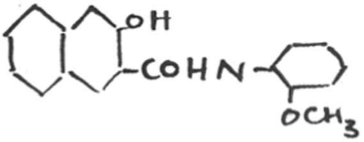
(VIII)

has been prepared by condensing α-furoyl chloride (XIX)

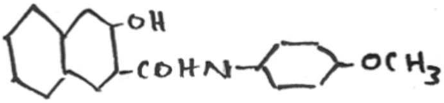


with Mono $\overset{N}{|}$B-hydroxy-3-naphthoyl-*m*-phenylenediamine. This naphthol is characterised by good substantivity as 2 evidenced by the deep shades available from it in combination with Fast Red Salt TR (5-chloro-2-aminotoluene) and Fast Blue Salt BB (4-benzoylamido-2:5-diethoxyaniline). The dyeings were characterised by very good fastness to kier-boiling and light, but the fastness to rubbing was a grade inferior to those containing the paraffin chain.

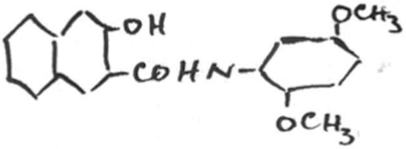
Introduction of methoxy groups confers increased substantivity and improved rubbing fastness. Naphtols AS-OL (2-hydroxy-3-naphthoyl-*o*-anisidide),



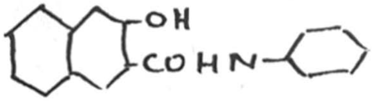
Naphtol AS-RL (2-hydroxy-3-naphthoyl-*p*-anisidide



and Naphtol AS-BG (2-hydroxy-3-naphthoyl-2:5-dimethoxyanilide)



give dyeings faster in every respect than Naphtol AS

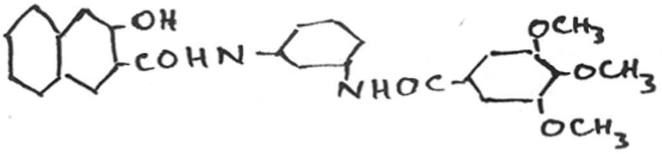


this superiority being ascribed to the presence of the methoxyl groups.

Naphthol (IX)

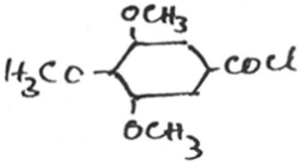
Cf. m & p- benzoylamido

Try p-nitrobenzoic acid



(IX)

has now been synthesised by condensing mono-N-2-hydroxy-3-naphthoyl-*m*-phenylenediamine with trimethyl galloyl chloride



(XX)

The naphthol was characterised by poor tinctorial power. The fastness to rubbing was good, but in view of the weak shade, this is illusory.

Purification of the naphthols synthesised in this series was effected by dissolving them with the aid of alcohol and caustic soda, filtering and precipitating with hydrochloric acid. The precipitate was collected at the pump, washed free from acid and dried.

Dye trials using these new naphthols were carried out using Fast Red Salt TR and Fast Blue Salt BB. Kier-boiling was carried out in the small high pressure kier described by Dhingra, Uppal and Venkataraman (J. Soc. Dyers Col., 1937, 53, 91), the dyed yarn being affixed to grey cloth in imitation of coloured sarees. Fastness to light was determined by methods elaborated by Bhat and Ramachandran (J. Ind. Chem. Soc., Indl. Ed., 1942, 5, 11).

Nitrogen estimations were carried out by the micro-Kjeldahl method in the Pregl apparatus (Quantitative Organic Micro-Analysis by F. Pregl, translated by E. Fyleman, second edition, 1930, p. 109). In the case of the nitro compounds ~~and~~ cellulose in sulphuric acid was used as the reducing agent (cf. Forster, Mehta and Venkataraman, loc. cit. ~~and Bhat~~).

EXPERIMENTAL

Preparation of 2-hydroxy-3-naphthoyl chloride was carried by the method described by Bhat, Forster and Venkataraman (J. Soc. Dyers Col., 1940, 56, 166) and which consisted in heating equal parts of 2-hydroxy-3-naphthoic acid and thionyl chloride over a water bath for about 5 hours in the presence of a solvent like petroleum ether (b.p. 60-70°C.) filtering and allowing the acid chloride to crystallise out in yellow needles, m.p. 96°C. Condensations with the various amines were effected by heating the acid chloride and the amine over an oil bath for 2 hours in the presence of a solvent like solvent naphtha and allowing the reaction product to settle and filtering off. Wherever the yield happened to be poor, steam distillation of the filtrate was effected.

Mono-N-2-hydroxy-3-naphthoyl-m-phenylenediamine

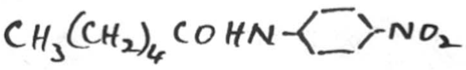
Name
m-[illegible] comps

used in a few condensations was prepared by taking pure Naphtol AS-BS (2-hydroxy-3-naphthoyl-m-nitranilide) (30 g.) in hot water (230 c.c.), acidified with glacial acetic acid (7 c.c.), iron filings (30 g.) being slowly introduced and the whole being refluxed for 3 hours, more hot water (230 c.c.) being added gradually during refluxing. Filtration and concentration of the aqueous filtrate gave a poor yield. The iron oxide sludge was extracted twice with absolute alcohol using 200 c.c. each time and these extracts mixed with the aqueous one. The amine which crystallised out was recrystallised from dilute alcohol and gave ~~a~~ yellow plates, m.p. 193°C. (cf. Turski, B.P. 347,609).

Caproyl chloride $CH_3(CH_2)_4COCl$:

To caproic acid (20 g.) in a Geissler flask, provided with an air condenser and calcium chloride tube, was added phosphorus trichloride (10 c.c.) and heated over a water bath for one hour. The supernatant caproyl chloride was collected by decontation.

Caproyl-p-nitranilide (XV):



(XV)

Caproyl chloride (15 g.) was added to *p*-nitraniline (16 g.), dissolved in dry distilled pyridine (30 c.c.), heated over a water bath for 2 hours and left overnight. On pouring to ice and hydrochloric acid, an oily yellow product separated which was washed free from acid and treated with sodium carbonate to remove the unreacted fatty acid. It was finally crystallised from dilute acetic acid in pale yellow needles (18.3 g.), m.p. 53-55°. (Found: N, 11.6. $C_{12}H_{16}O_3N_2$ requires N, 11.8%).

Mono-N-caproyl-p-phenylenediamine (X):

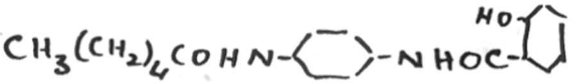
(X)

To caproyl-*p*-nitranilide (18 g.) was added hot water (150 c.c.) containing glacial acetic acid (12 c.c.) and iron filings (18 g.) in small lots at a time and the contents refluxed for 3 hours, and the product filtered and the filtrate concentrated to a small bulk. The iron oxide sludge was extracted twice with absolute alcohol and the extracts mixed together. The amine (8.3) which

s

separated out was dried and used directly for condensation with 2-hydroxy-3-naphthoyl chloride. new ?

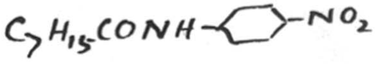
N-2-Hydroxy-3-naphthoyl-N'-caproyl-p-phenylenediamine (I):



(I)

2-Hydroxy-3-naphthoyl chloride (7.5 g.) dissolved in solvent naphtha (75 c.c.) was mixed with mono-N-caproyl-p-phenylenediamine (8.3 g.) also dissolved in the same solvent and heated on an oil bath at 150°C. for 2 hours. The product that settled down (9.2 g.) was collected and purified. It crystallised from acetylene tetrachloride as pale cream coloured crystalline powder, m.p. 255-6°C. (Found: N, 7.8. $C_{23}H_{24}O_3N_2$ requires N, 7.4%). It gave a greyish blue with alcoholic ferric chloride. 2

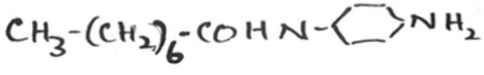
Caprylyl-p-nitranilide (XVI):



(XVI)

Caprylyl chloride (cf. Aschan, Ber., 1898, 31, 2348) (10 g.) dissolved in dry pyridine (30 c.c.) was mixed with p-nitraniline (8.5 g.) also dissolved in the same solvent, heated for 2 hours and left overnight. The product obtained on pouring into ice and hydrochloric acid was treated with sodium carbonate and crystallised from alcohol in light canary yellow needles (12.2 g.). 3 It melted at 70-72°C. (Found: N, 10.3. $C_{14}H_{20}O_3N_2$ requires N, 10.6%).

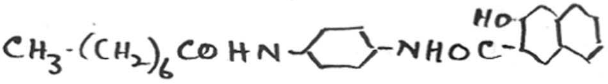
Mono-N-caprylyl-p-phenylenediamine (XI):



(XI)

Mono-N-caprylyl-p-phenylenediamine (6.4 g.) was obtained by reducing caprylyl-p-nitranilide (9.0 g.) with iron and acetic acid as previously described. It crystallised from dilute alcohol in pale brown needles 4 melting at 97-98°C. (Found: N, 11.7. $C_{14}H_{22}ON_2$ requires N, 11.9%).

N-2-Hydroxy-3-naphthoyl-N'-caprylyl-p-phenylenediamine (II):



(II)

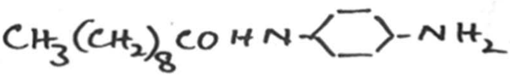
To mono-N-caprylyl-p-phenylenediamine (5 g.) in solvent naphtha (40 c.c.) was added 2-hydroxy-3-naphthoyl chloride (4.1 g.) dissolved in the same solvent and heated on oil bath for 2 hours. The precipitate obtained on cooling was washed with benzene and the naphthol recovered by filtration. The purified product (3.2 g.) crystallised from acetylene tetrachloride. The pale brown crystalline powder melted at 251-52°C. (Found: N, 7.1. $C_{25}H_{28}O_3N_2$ requires N, 6.9%). The alcoholic solution gave an olive green colouration with ferric chloride.

Capryl-p-nitranilide (XVII):

(XVII)

Capryl chloride (10 g.) dissolved in dry pyridine (30 c.c.) was mixed with p-nitraniline (7.2 g.) also dissolved in the same solvent and left overnight. On pouring into ice and hydrochloric acid a pale yellow product separated, which was treated with sodium carbonate and crystallised from alcohol in pale brownish yellow needles. The product (14.8 g.) melted at 90-91°. (Found: N, 9.4. $C_{16}H_{24}O_3N_2$ requires N, 9.6%).

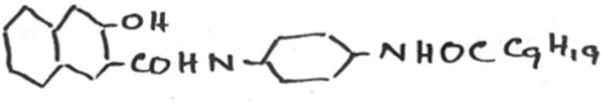
Mono-N-capryl-p-phenylenediamine (XII):



(XII)

Capryl-p-nitranilide (12 g.) was reduced with iron and acetic acid in the usual manner. The product (7.3 g.) crystallised from alcohol in brown needles, melting at 105-106°. (Found: N, 10.3. $C_{16}H_{26}ON_2$ requires N, 10.6%).

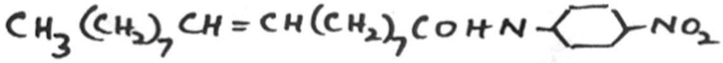
N-2-Hydroxy-3-naphthoyl-N'-capryl-p-phenylenediamine (III):



(III)

Mono-N-capryl-*p*-phenylenediamine (5.2 g.) in solvent naphtha (40 c.c.) was mixed with 2-hydroxy-3-naphthoyl chloride (4.1 g.) and heated over an oil bath for 2 hours. The reaction product that settled down was collected at the pump (3.7 g.). It crystallised from acetylene tetrachloride in small needles, melting at 246°. (Found: N, 6.3, $C_{27}H_{32}O_3N_2$ requires N, 6.5%). It gave a bluish green colouration with ferric chloride.

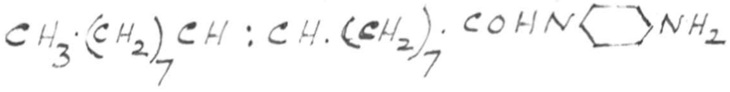
Oleyl-p-nitranilide (XVIII):



(XVIII)

Oleyl chloride (cf. Aschan, *Ber.*, 1898, *31*, 2349) (18 g.) was added to a solution of *p*-nitraniline (8.3 g.) dissolved in pyridine (45 c.c.), heated over a water bath for 2 hours and left overnight. The product obtained on pouring into ice and hydrochloric acid was found to be oily. It was taken up in ~~a~~ether and washed repeatedly with dilute hydrochloric acid to free from pyridine washed free from acid and dried in the desiccator. It remained mainly as a highly viscous oily mass of golden yellow colour (14.6 g.). (Found: N, 7.3. $C_{24}H_{38}O_3N_2$ requires N, 7.0%).

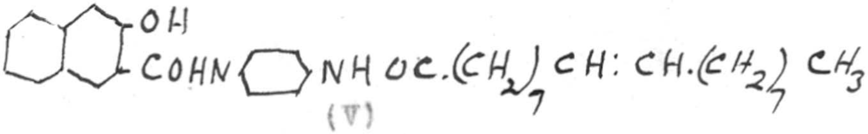
Mono-N-oleyl-p-phenylenediamine (XIV):



(XIV)

Oleyl-p-nitranilide (10 g.) was reduced by the usual method to yield the amine (6.9 g.). This crystallised from dilute alcohol in pale brown coloured needles which set to a semi solid mass on attempting to isolate. It gave a melting point 67-69°. (Found: 10 N, 7.3. $C_{22}H_{40}ON_2$ requires N, 7.5%).

N-2-Hydroxy-3-naphthoyl-N'-oleyl-p-phenylenediamine (V):

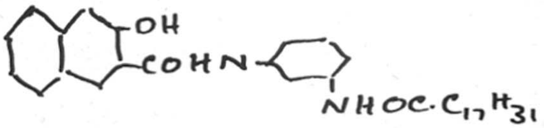


(V)

~~2.9 g.~~

2-Hydroxy-3-naphthoyl chloride (2.9 g.) in solvent naphtha (50 c.c.) was added to mono-N-oleyl-p-phenylenediamine (5.2 g.) also dissolved in the same solvent and refluxed for 2 hours at 150°C. The product separating out on cooling was collected by filtration. The naphthol (3.8 g.) crystallised from acetylene tetrachloride in pale grey crystalline powder, m.p. 236-37°C. (Found: N, 4.9. $C_{35}H_{46}O_3N_2$ requires N, 5.2%). It gave a green colouration with ferric chloride.

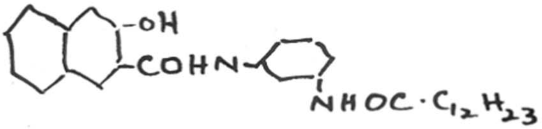
N-2-Hydroxy-3-naphthoyl-N'-linseedyl-m-phenylenediamine(VI):-



(VI)

To linseedyl chloride (10 g.) prepared in the usual way, was added mono-2-hydroxy-3-naphthoyl-m-phenylenediamine (9.3 g.) dissolved in solvent naphtha (50 c.c.) and processed in the usual way. The cream coloured product (8.4 g.) crystallised from acetic acid as crystalline powder melting at 185-86°C. (Found: N, 5.4. $C_{35}H_{44}O_3N_2$ requires N, 5.2%). It gave an olive green colouration with ferric chloride.

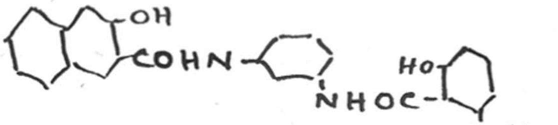
N-2-Hydroxy-3-naphthoyl-N'-naphthenyl-m-phenylenediamine (VII):



(VII)

Mono-2-hydroxy-3-naphthoyl-m-phenylenediamine (7 g.) dissolved in solvent naphtha (75 c.c.), was refluxed for 2 hours with naphthenyl chloride (5 g.) also dissolved in the same solvent. The yellow coloured product that separated on cooling was collected at the pump. Filtration was slow due to the sticky nature of the product. It was treated first with petroleum ether (b.p. 60-70°), then with alcohol to remove any unreacted naphthenic acid and finally with dilute hydrochloric acid to remove any free base. It crystallised from glacial acetic acid as yellow crystalline powder (5.2 g.) melting at 183-84°.
13 (Found: N, 5.7. $C_{30}H_{36}O_3N_2$ requires N, 5.9%). It gave a bluish green colouration with ferric chloride.

Mono-N-2-hydroxy-3-naphthoyl-N'-tetrahydroanacardyl-m-phenylenediamine (IV):



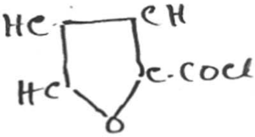
(IV)

The acid chloride of tetrahydroanacardic acid was prepared by refluxing tetrahydroanacardic acid (3 g.) in petroleum ether (b.p. 60-70°) (25 c.c.) and thionyl chloride (5 c.c.) over a water bath for 2 hours. The resultant viscous acid chloride was directly taken up for condensation.

Tetrahydroanacardyl chloride (3 g.) was dissolved in dioxan (30 c.c.) and to this was added mono-N-2-hydroxy-3-naphthoyl-m-phenylenediamine (2.5 g.) and the contents heated over a water bath for 3 hours. The brownish product that settled down on cooling was collected at the pump and the filtrate poured into cold water. More of the substance was separated out. This was added to the residue obtained by filtration. This crystallised from acetic acid in cream coloured plates which did not melt below 300°C. (Found: N, 4.3.

$C_{39}H_{48}O_4N_2$ requires N, 4.6%). It gave a greyish blue colouration with ferric chloride).

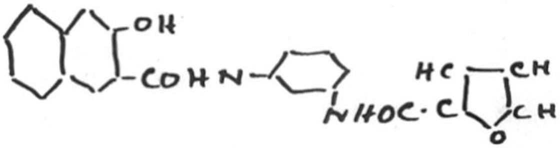
Furoyl chloride (XIX):



(XIX)

Furoic acid (5 g.) was refluxed with thionyl chloride (50 c.c.) for 3 hours over a water bath, the excess thionyl chloride removed by distillation under vacuum. The resultant furoyl chloride was used directly for condensation with mono-N-2-hydroxy-3-naphthoyl-*m*-phenylene diamine.

N-2-Hydroxy-3-naphthoyl-N'-furoyl-m-phenylene-diamine (VIII):

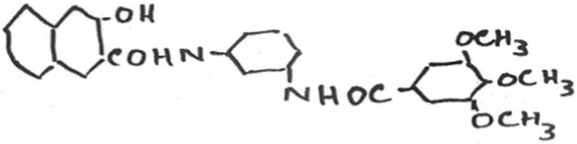


(VIII)

Furoyl chloride (5 g.) was condensed with N-2-hydroxy-3-naphthoyl-~~N'~~-*m*-phenylenediamine (10.7 g.)

dissolved in solvent naphtha (75 c.c.). The resultant brownish grey product (9.8 g.) was purified in the usual way. It crystallised from dilute acetic acid in rectangular cream coloured plates melting at 220-221°C. With ferric chloride it gave a green colouration. (Found: N, 7.4. $C_{22}H_{16}O_4N_2$ requires N, 7.5%).

N-2-Hydroxy-3-naphthoyl-N'-trimethylgalloyl-m-phenylenediamine (XIX):



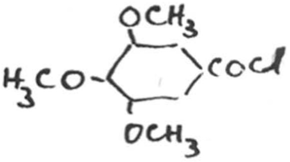
(XIX)

Trimethylgalloyl chloride (3 g.) was dissolved in nitrobenzene (30 c.c.). To this was added mono-N-2-hydroxy-3-naphthoyl-m-phenylenediamine (4.3 g.) and anhydrous sodium acetate (4.5 g.) and the contents of the flask refluxed for 3 hours at 250°C. A small quantity of greyish brown product that settled down was filtered off and the filtrate steam distilled. The substance recovered by steam distillation appeared more deep in colour than the first. The product (6.2 g.)

was boiled with water to remove any trimethyl gallic acid and then treated with hydrochloric acid to eliminate the unreacted amine. The naphthol thus recovered was purified in the usual way. It crystallised from a mixture of acetylene tetrachloride and benzene in tiny pale grey coloured needles, which did not melt below 330°. (Found: N, 6.3. $C_{27}H_{24}O_6N_2$ requires N, 6.0%).

Gallic acid was first methylated by the usual method (cf. "Organic Syntheses, Collective Volume I, p. 522, 1932). It crystallised from water in colourless needles melting at 167°C.

Trimethylgalloyl chloride (XX):



(XX)

Trimethylgallic acid (5 g.) (1 mol.) was mixed with thionyl chloride (10 g.) (3.5 mols.) and refluxed for 3 hours. The excess thionyl chloride was removed by distillation under vacuum and the resultant acid chloride crystallised from petroleum ether (b.p. 90-100°) and dried under vacuum in a desiccator. It melted at 78°C.

Dye trials:

No difficulty was experienced in effecting dissolution of any of the naphthols synthesised in this series. Although it was noticed that both the "hot" and the "cold" methods could be used with ease, in practice it was found advantageous to adopt a combination of both the methods to effect dissolution. The advantage lay in the fact of rapid manipulation with clearer resultant solutions. Impregnation was carried out for 15 minutes at room temperature (30°C.) on single 20's bleached yarn, in a material liquor ratio of 1:20. At the end of the period, the material was removed, hydroextracted and split into two parts; one part was developed in a 3% solution of Fast Red Salt TR and the other in Fast Blue Salt BB, each containing 1% Diazopon A (on volume), washed in cold water and soaped at the boil for 15 minutes using 0.8% soap solution, washed and dried.

Method of dissolving the naphthols: The naphthol (2 g.) was pasted up with methylated spirit (5 c.c.) and to this was added caustic soda (32.5%) (2 c.c.). Stirring of this was done for about 5 minutes when a clear solution resulted. This was poured in a thin stream with constant stirring, into warm water (150 c.c.) containing caustic soda (3 c.c.) and Turkey Red oil (4 c.c.). Keeping aside a few minutes led invariably to a clearer solution. It was then bulked up to (200 c.c.) with cold water. Impregnation was carried out for 15 minutes at room temperature (30°C.) on single 20's bleached yarn, in a material liquor ratio of 1:20. At the end of the period, the material was removed, hydroextracted and split into two parts and developed in a 3% solution of Fast Red Salt TR and Fast Blue Salt BB, containing 1% Diazopon A (on volume), washed in cold water and soaped at the boil for 15 minutes using 0.8% soap solution, washed and dried. In Table I are recorded observations as regards the colour of the naphthol solution and the colour on yarn, while in Table II the shades obtained by development with Fast Red Salt TR and Fast Blue Salt BB.

Tables/I and II

Table I

Naphthol	Base combined with -hydroxy-naphthoic acid	Colour of solution	Colour of yarn
I	Mono-N-caproyl-p-phenylenediamine	Pale olive yellow	Olive yellow
II	Mono-N-caprylyl-p-phenylenediamine	Brownish yellow	Olive yellow
III	Mono-N-capryl-p-phenylenediamine	Yellow brown	Yellow
IV	Mono-N-tetrahydroanacardyl-m-phenylenediamine	Brown	Yellow
V	Mono-N-oleyl-p-phenylenediamine	Yellow	Lemon yellow
VI	Mono-N-linseedyl-m-phenylenediamine	Light brown	Lemon yellow
VII	Mono-N-naphthenyl-m-phenylenediamine	Orange	Light yellow
VIII	Mono-N-furoyl-m-phenylenediamine	Deep brown	Brownish yellow
IX	Mono-N-trimethylgalloyl-m-phenylenediamine	Deep reddish brown	Yellow brown.

Table II

Naphthol	Base combined with -hydroxy-naphthoic acid	Shade Fast Red Salt TR	Shade Fast Blue Salt BB
I	Mono-N-caproyl-p-phenylenediamine	Cherry	Pansy
II	Mono-N-caprylyl-p-phenylenediamine	Lighter cherry	Lighter pansy
III	Mono-N-capryl-p-phenylenediamine	Deep blossom pink	Deep heliptrope
IV	Mono-N-tetrahydroanacardyl-m-phenylenediamine	Light pink	Purplish grey
V	Mono-N-oleyl-p-phenylenediamine	Deep malmaison rose	Light violet
VI	Mono-N-linseedyl-m-phenylenediamine	Straw berry pink	Deep lilac
VII	Mono-N-naphthenyl-m-phenylenediamine	Bluish pink	Heliotrope
VIII	Mono-N-furoyl-m-phenylenediamine	Cardinal	Deep reddish blue
IX	Mono-N-trimethylgalloyl-m-phenylenediamine	Light red	Light greyish blue

Kier-boiling:

Kier-boiling was carried out in the small pressure kier described by Dhingra, Uppal and Venkataraman (J. Soc. Dyers and Col., 1937, 53, 91). Imitation "sarees" were made using grey long cloth, the dyed yarn from each sample of naphthol synthesised, constituting the coloured border. Desizing of the "sarees" was effected by steeping the material overnight in a 0.25% solution of Viveral E Conc. to which an addition of 1% common salt (on volume) was made. Initially the desizing bath was maintained for a period of 3 hours at 50°C. and then ~~e~~in the cooling bath for the rest of the period. The "sarees" were removed, washed thoroughly in cold water and processed in the kier for 6 hours at 70°C. using a concentration of 1.5% soda ash (on weight of material used), washed and dried. The grading of the samples was then done by visual method as suggested by Forster, Mehta and Venkataraman (J. Soc. Dyers Col., 1938, 54, 209). The fastness grade and change in shades are recorded in Table III.

Table III

Naphthol	Base combined with -hydroxynaphthoic acid	Fastness to kier-boiling			
		Fast Red Salt TR		Fast Blue Salt BB	
		Shade after kier-boiling	Kier-boiling fastness grade	Shade after kier-boil	Kier-boiling fastness grade
I	Mono-N-caproyl-p-phenylenediamine	Bluer and slightly duller than original. No appreciable loss of depth	4-5	No change in tone or depth	5
II	Mono-N-caprylyl-p-phenylenediamine	No change in tone. Slight loss in depth	4	No change in tone. Slight loss in depth	4
III	Mono-N-capryl-p-phenylenediamine	No change in tone. Very slight loss in depth	4-5	No change in tone. Very slight loss in depth	4-5
IV	Mono-N-tetrahydroanacardyl-m-phenylenediamine	No change in tone. Loss in depth	3	No change in tone. Loss in depth	3
V	Mono-N-oleyl-p-phenylenediamine	Appreciable loss in depth. No change in tone	3	No change in tone	3

Table III contd.

Naphthol	Base combined with -hydroxy-naphthoic acid	Fastness to kier-boiling Fast Red Salt TR Shade after kier-boiling	 Kier-boiling fastness grade	 Fast Blue Salt BB Shade after kier-boiling	 Kier-boiling fastnes grade
VI	Mono-N-linseedyl-m-phenylenediamine	Appreciable loss in depth. No change in tone	3	No change in tone	3
VII	Mono-N-naphthenyl-m-phenylene-diamine	Appreciable loss in depth. No change in tone.	3	No change in tone	3
VIII	Mono-N-furoyl-m-phenylenediamine	Slightly bluer and weaker than original	4	Slightly weaker. No change in tone	4-5
IX	Mono-N-trimethylgalloyl-m-phenylenediamine	Appreciable loss in depth	3	Appreciable loss in depth.	3

Advantages of the introduction of a long chain saturated fatty acid amide group in the p- or m- position to the naphthoylamido group was demonstrated by the high fastness grade of naphthols(I), (II) and (III). The presence of unsaturated linkages appear to be a disadvantage as evidenced by the inferior fastness of naphthols (IV), (V), (VI) and (VII). Heterocyclic rings in a naphthol nucleus led to increased substantivity and good fastness to kier-boiling, as was shown by naphthol (VIII), the dyeing from which was not only characterised by depth of shade, but also by high grade of fastness (4-5). Acylation of an amino group by an acid having heterocyclic structure would therefore prove to be an advantage.

As between the combination with Fast Red Salt TR and Fast Blue Salt BB, the advantage always was in favour of the latter, due evidently to the presence of the benzamido and alkoxy groups in Fast Blue Salt BB.

Fastness to rubbing:

Rubbing fastness tests were carried out according to methods described by Forster, Ramachandran and Venkataraman (J. Soc. Dyers Col., 1938, 54, 216), in which the padded revolving arms of a Kleinewefer mercerising machine provided the necessary movement of the yarn, the tension of the latter being adjusted by shifting the movable arm to the desired position. A stout wooden shoe, the curvature of the underside of which corresponded to the convexity of the roller surface and was padded with an inner layer of flannel and an outer layer of bleached drill with the twill side in immediate contact with the yarn, the roughness of the twill facilitating maximum rubbing. The shoe was suspended from the centre of a lever, one end of which was supported by the frame work of the machine and a 6-lb. weight was suspended from the other end. Rubbing was carried out for 5 minutes and from the intensity of the streaks obtained, and comparing against the rubbing obtained in the case of the standards, the dyeings were graded for rubbing fastness.

Standard dyeings adopted were the following; the figures within brackets referring to their grades on the basis of nitrogen assay before and after rubbing: Naphtol AS and Fast Blue Salt BB (2); Naphtol AS-SW and Fast Red Base RBE (3); Naphtol AS-OL and Fast Red

Salt TR (4); Naphtol AS-RL and Variamine Blue Salt B (5); and Naphtol AS-SG and Fast Red Salt B (6), representing a loss of nitrogen of 16-20; 13-15; 6-12; 2-5 and less than 2% respectively. Wherever the nitrogen assay was not quite conclusive, or not carried out, as for instance in the case of grade 6 (Naphtol AS-SG and Fast Red Salt B) reliance was placed on visual observation. In Table IV are given the fastness grades of the dyeings.

Table IV/

Table IV

Naphthol	Base combined with -hydroxy-naphthoic acid	Rubbing fastness grade	
		Fast Red Salt TR	Fast Blue Salt BB
I	Mono-N-caproyl-*p*-phenylenediamine	4-5	4-5
II	Mono-N-caprylyl-*p*-phenylenediamine	4-5	4-5
III	Mono-N-capryl-*p*-phenylenediamine	4-5	4-5
IV	N-Tetrahydroanacardyl-*m*-phenylenediamine	4-5	4-5
V	Mono-N-oleyl-*p*-phenylenediamine	4	4
VI	Mono-N-linseedyl-*m*-phenylenediamine	4	4
VII	Mono-N-naphthenyl-*m*-phenylenediamine	4	4
VIII	Mono-N-furoyl-*m*-phenylenediamine	3-4	3-4
IX	Mono-N-trimethylgalloyl-*m*-phenylenediamine	4-5	4-5

The rubbing fastness of the dyeings from the naphthols synthesised in this series, barring naphthol (VIII) (the α-furoic acid derivative)was good, indicating the beneficial effects due to the presence of a long chain fatty acid radicle. Any improvement in the rubbing fastness of a naphthol dyeing is known to depend to a large degree on the effective removal of the superficially precipitated dyestuff. Soap, the common detergent used in the after-treatment of naphthol dyed material, is according to Hartley (*loc. cit.*) exercises a solvent action on organic compounds. The introduction of a long paraffin chain, as in the case of the naphthols under discussion, was helpful, as organic compounds exhibit a tendency to dissolve in solvents having structural similarity to themselves. The high grade of fastness exhibited by naphthol (IX) is rather misleading. It is mainly due to the weak shade obtained and as such no safe conclusions could be drawn from it.

The derivatives containing unsaturated linkages, barring naphthol (IV), gave a slightly lower grade of fastness. This, however, does not represent any serious lowering of the grade and in any case it is no argument against the introduction of unsaturated linkages, as with a slightly prolonged treatment, the next higher grade could no doubt be reached.

Naphthol (VIII) exhibited only a moderate fastness to rubbing. Introduction of a heterocyclic structure in the naphthol nucleus therefore would not appear to have any special advantage as far as this fastness aspect is concerned, although in the absence of syntheses of more naphthols with similar structure along with their p- and m-analogues, no generalisations could be made. It should, however, be realised that rubbing fastness, as in the case of light, would depend to a certain extent on the depth of shade, which in the absence of special linkages as in naphthols (I), (II), (III), (IV) and (V) might lead to higher rubber. Naphthol (VIII) (α-furoic acid derivative) giving a shade with Fast Red Salt TR and Fast Blue Salt BB much deeper than any of the foregoing, might account for the slightly inferior grade. Experiments are in progress to synthesise more naphthols of this type with the acidamide group in the p- and o- positions to the naphthoylamido group and to study the fastness properties of dyeings obtained from them.

Fastness to light:

Fastness to light was determined by methods described by Bhat and Ramachandran (J. Ind. Chem. Soc., Indl. Ed., 1942, 5, 11). The dyed material was closely wound on thin cardboard 3 1/2" x 2 1/2" and mounted on to special metallic frames which allowed of half the sample being covered and the other half exposed suspended in the specially designed chamber of the Calico Printers' Association's Fadeometer. In the latter the source of light is an enclosed carbon arc surrounded by a single annular exposure chamber. The inside wall of the cylinder consisting of a double glass screen with water circulating between the glasses. The outside wall is also water cooled. The air in the chamber is humidified by means of a heatable water tray forming the bottom of the apparatus, with a fan revolving over the surface of the water. These devices allow the temperature and relative humidity of the atmosphere surrounding the samples to be controlled and regulated. The relative humidity in the chamber was maintained at 80%. The samples were examined at frequent intervals and removed as soon as there was visible fading.

From the figures obtained fastness grades were assigned on the basis of the data furnished by Bhat and Ramachandran (*loc. cit.*). In Table V are mentioned the fastness grades.

Table V

Naphthol	Base combined with -hydroxy-naphthoic acid	Light fastness grade Fast Red Salt TR	Light fastness grade Fast Blue Salt BB
I	Mono-N-caproyl-*p*-phenylenediamine	5-6	4-5
II	Mono-N-caprylyl-*p*-phenylenediamine	4-5	4-5
III	Mono-N-capryl-*p*-phenylenediamine	4-5	2-3
IV	Mono-N-tetrahydroanacardyl-*m*-phenylenediamine	2-3	2-3
V	Mono-N-oleyl-*p*-phenylenediamine	4-5	4-5
VI	Mono-N-linseedyl-*m*-phenylenediamine	2-3	2-3
VII	Mono-N-naphthenyl-*m*-phenylenediamine	2-3	2-3
VIII	Mono-N-furoyl-*m*-phenylenediamine	4-5	6-7
IX	Mono-N-trimethylgalloyl-*m*-phenylenediamine	2-3	2-3

Barring naphthols (V) and (VI) and the Blue BB combination of naphthol (III), all the others exhibited good fastness to light. In view of the beneficial effects which the alkoxy group is known to exert towards fastness to light, the poor fastness of the Blue BB combination in the case of naphthol (III) is inexplicable. Light fastness is known to depend on depth of shade and the anomaly may be explained by inferior depth of shade obtained in the case of naphthol (III) as against (I) and (II). The same explanation could be given for the poor fastness exhibited by naphthol (IX). Methoxy groups are known to introduce increased fastness to light as evidenced by the higher fastness grades of combinations with Naphtol AS-RL (2-hydroxy-3-naphthoyl-p-anisidide) and Naphtol AS-BG (2-hydroxy-3-naphthoyl-2:5-dimethoxyanilide) over Naphtol AS (2-hydroxy-3-naphthoylanilide). Naphthol (IX) gave very poor shades, hence the poor fastness to light.

Plurality of double bonds, though conferring beneficial effects as regards solubility, would not appear to be a favourable factor as regards fastness to light. Naphthols (IV), (VI) and (VII) exhibited only poor fastness to light as against naphthol (V) (the oleic acid derivative) which gave a grade 4-5, i.e. good.

Naphthol (VII) is remarkable for the high fastness exhibited by both the combinations. As between Red TR and Blue BB, the latter shows up to great advantage, due to the admittedly beneficial effects of the alkoxy group present in the latter.

Part II

Dyes derived from cashew nut shell oil.

INTRODUCTION

Cashew nut is the fruit of an ever green tree, Anacardium occidentale Linn., which is indigenous to Central and South America, but believed to have been introduced into this country by the Portuguese. It is valued partly on account of its gum (cashew gum), claimed to be a substitute for gum arabic, its fruit, which has a pleasant taste, and above all, for its seed originally valued for the kernel and now priced highly for the oil extruded from the shells. This oil has been used, in view of its known protective action, to coat boats, floors and rafters against the ravages of white ants.

Staedeler (Das Annelen der Chemie und der pharmacie, 1884, 63, 137) attempted to study the chemical composition of the oil. He isolated two constituents, one an acid, which he termed "anacardic acid", constituting

90% of the oil, and the remaining 10% was termed "cardol", a substance mainly phenolic in character. Ruheman and Skinner (*J. Chem. Soc.*, 1887, *51*, 663; *Ber.*, 1887, *20*, 1861) and Sudborough (*J. Ind. Inst. Sc.*, 1923, *5*, 133; *Chem. Abs.*, 1923, *17*, 1897) indicated that anacardic acid was a hydroxycarboxylic acid and gave it the molecular formula $C_{22}H_{32}O_2$. The isolation and hydrogenation of anacardic acid and its decarboxylation products were carried out by Smit (*Proc. Acad. Sc. Amsterdam.*, 1931, *34*, 165), who considered anacardic acid to be a homologue of salicylic acid having an alkyl chain $C_{15}H_{27}$, attached to the nucleus. Pillay (*J. Ind. Chem. Soc.*, 1935, *12*, 226) considered that the alkyl chain was *ortho* to the hydroxyl, but this has been disputed by Gokhale, Patel and Shah (*Curr. Sci.*, 1940, *9*, 363), who claimed the *meta* position for the alkyl group and proved this by preparing the tribromo product of tetrahydroanacardol, while the *ortho* and *meta* products would give only dibromo compounds. The carboxyl lies in all probability between the hydroxyl and the alkyl groups in view of the difficulties experienced in direct esterification.

Extraction of cashew nut oil has been mainly confined to the hot roasting process and the oils as marketed appear as highly viscous, not much varying in colour ~~from~~ all appearing as deep brown coloured products, containing tarry and other impurities. The anacardic acid contents of these oils have been generally stated to be very high, as much as 90%. Patel and his co-workers (J. Ind. Inst. Sci., 1922, 5, 152) obtained the oil by extraction with ether and claimed that, as against the commercial oils (extracted by hot methods), the former contained anacardic acid to the extent of 90%, while the latter gave a value of 16%. The present author has made a study of the oils obtained by various methods of extraction, viz., extraction with solvents (alcohol) in the cold and in hot, by pressing in an oil press, extraction of the residual shells with alcohol, as also a few samples obtained from a variety of sources known to employ hot methods, for their anacardic acid contents, and he could not confirm the results claimed by Patel and his co-workers. In assaying the anacardic acid contents, the simple titration method against cuastic soda, the oil being dissolved in neutral alcohol, was adopted. Of the eight samples examined by the author, none was found to give a value more than 60%, and curiously enough, the cold extracted oils gave a lower percentage than the hot extracted commercial ones, although among the latter there were samples giving a value as low as 7%. The results are recorded in Table I of the experimental part.

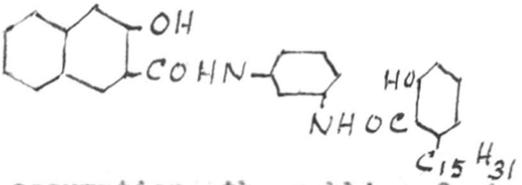
Cashew nut oil has now considerable commercial significance as a raw material for various synthetic schemes. Harvey was the first to use this oil in the manufacture of varnishes and impregnating materials known as "Harvel", "Oilstop" and "Cardolite". Its commercial utility is based on its ability to polymerise when heated at 100-200° with an acid or an alkaline catalyst, and formation of condensation products with aldehydes, because of its phenolic constituents. Harvey's numerous patents (*U.S.P.* 1,725,724; 1,725,793, 1,725,795; 1,977,826; *Can. P.* 285,183; *U.S.P.* 1,771,785; 1,771,786 and *B.P.* 272,509) make claims for the use of the oil as a substitute for shellac, a quick drying coating material, as substitute for rubber, as plasticiser for cellulose products, sulphur, resins, rubber and waxes and also as a water proofing agent.

Anacardic acid, the essential constituent of cashew nut oil, has marked wetting and detergent properties (Venkataraman, *Curr. Sci.*, 1939, *8*, 282; Gandhi and Venkataraman, *ibid.*, 367). The *ortho*-hydroxycarboxylic acid structure and ethylenic bonds in this acid would lead to good substantivity, and its long paraffin chain residue would lead to better rubbing fastness of the azoic dyes from naphthols containing the anacardic acid residue. The materials processed with these dyes will be less liable to mildew attack in view of the bactericidal and insecticidal properties of anacardic acid and its derivatives (cf. Gandhi and Venkataraman, *loc. cit.*).

The structural similarity of anacardic acid to salicylic acid was utilised by Gandhi (Ph.D. Thesis, Bombay Univ., 1941) to prepare a series of antiseptics to be used in textile processing. It was anticipated that the sodium salts of this acid would also behave as a good wetting agent. Its poor resistence to hard water, however, allows only of restricted scope in this direction.

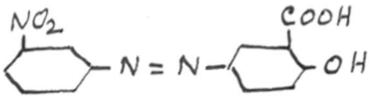
[illegible]

As a substitute for salicylic acid in the manufacture of dyes, anacardic acid should prove useful. Its long aliphatic chain should also prove helpful in getting dyeings with good resistance to rubbing if anacardic residue were introduced in a naphthol nucleus. Naphthol (IV) (Part I of this thesis) where the condensation has been effected between mono-N-tetrahydroanacardyl m-phenylenediamine and β-hydroxynaphthoyl chloride to produce



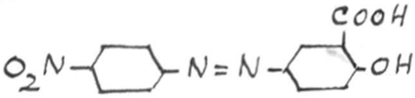
has justified the assumption, the rubbing fastness grade of the dyeing with Fast Red Salt TR and Fast Blue Salt BB being (4-5). The advantages of the introduction of alkyl chains has been recognised to impart to wool dyes enhanced fastness to wet processing. The carbolan dyes of the I. C. I. contain incorporated in the dye nucleus alkyl groups containing C_4 to C_{20}, either directly attached to the dye nucleus or to a nitrogen atom or to oxygen or sulphur, as alkyl ethers or thioethers or to carboxylic acid as esters.

Azo-chrome mordant dyes have been prepared by utilising the laking effect of the carboxyl group with or without an o-hydroxy group. Secondary components employed among others, in their syntheses, are phenols such as β-naphthol, which give o-hydroxyazo compounds, salicylic and cresotinic acids. Alizarin Yellow GG

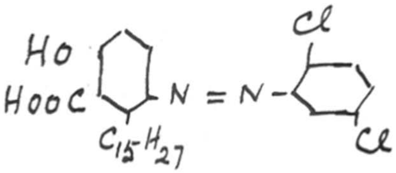


ll^{l} dgs
~~[illegible]~~
ICI method
of TR dg

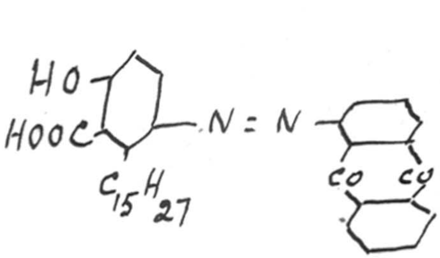
and Alizarine Orange R



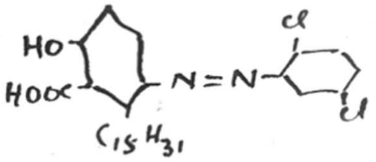
are prepared from diazotised m- and p-nitranilines and salicylic acid. Anacardic acid possessing an additional feature in the form of an aliphatic residue should, in view of the considerations aforementioned prove very useful. Compounds (V), (VI), (IX) and (XVIII) have been prepared



(V)

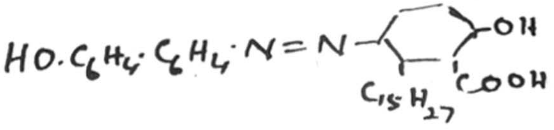


(VI)



(IX)

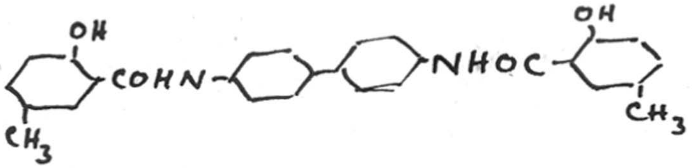
?



(XVIII)

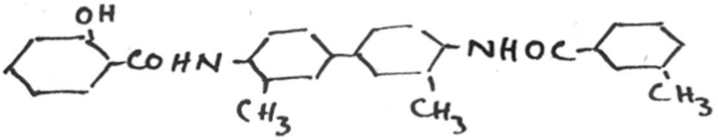
by coupling diazotised 2:5-dichloraniline, α-naphthylamine and benzidine with anacardic and tetrahydroanacardic acids.

The Society of Chemical Industry in Basle (The Ciba) have synthesised new types of Naphtols not based on the o-hydroxycarboxylic acid model. Typical of such attempts are the three valuable Ciba Naphtols SB, ST and SO

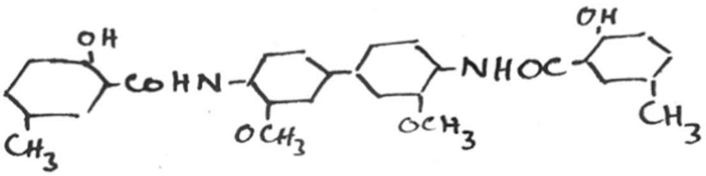


Study
Two
Try CH_3CO; Br;
of CH_3CONH
Couple in substance

Ciba Naphtol SB



Ciba Naphtol ST

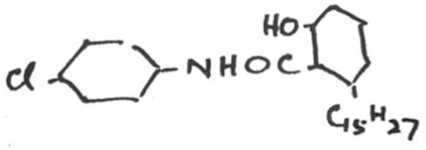


SD?

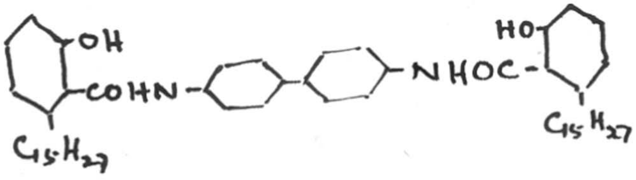
Ciba Naphtol SO

obtained by condensing 2 mols. of *p*-cresotinic acid (4-hydroxytoluene-3-carboxylic acid) with 1 mol. of benzidine, tolidine and dianisidine respectively (*F. P.* 727,003; *G.P.* 565,340) yielding useful deep brown shades when treated with suitable diazo salts. Cresotinic acid has structural similarity to anacardic acid and therefore should easily lend itself to similar syntheses. Since anacardic acid is cheap and available in abundance, these naphthols should be readily available. Anacardic and tetrahydroanacardic acids have now been condensed with bases such as β-chloraniline, benzidine, dehydrothiotoluidine, and mono-N-2-hydroxy-3-naphthoyl-*m*-phenylenediamine to produce compounds

Azo → NPD

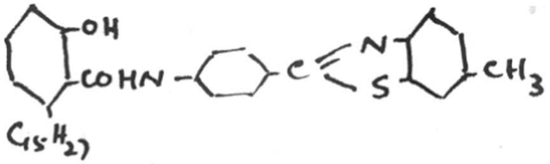


(I)

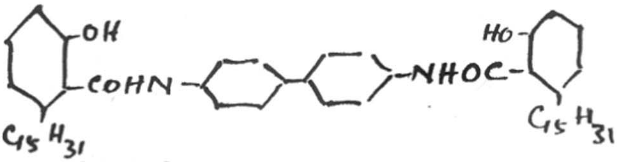


(II)

Genuine?



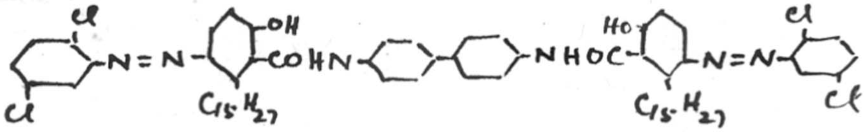
(VII)



(VIII)

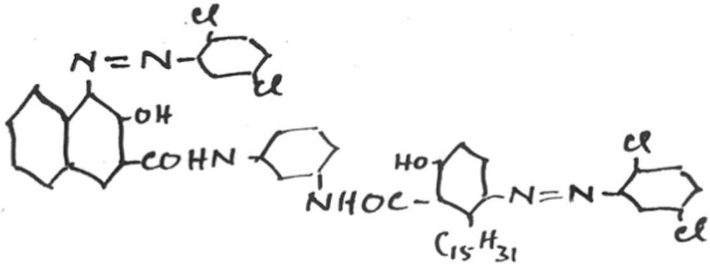
Azo dyes in substance have been prepared by coupling compound (II) with diazotised 2:5-dichloraniline to produce (IV)

Wool colours
Direct on colours



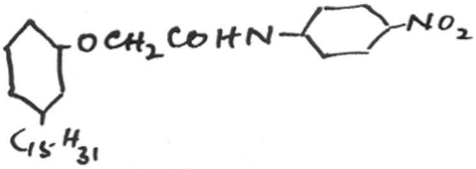
(IV)

and N-2-hydroxy-3-naphthoyl-N'-tetrahydroanacardyl-m-phenylenediamine with diazotised 2:5-dichloraniline to produce (XVI)



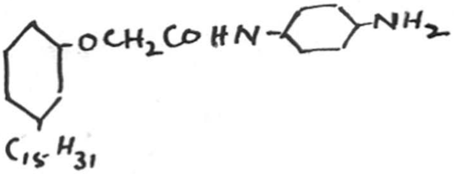
(XVI).

Other compounds prepared are (XII), (XIII), (XIV) and (XV) by condensing m-pentadecylphenoxyacetylchloride with p-nitraniline (XII)



(XII)

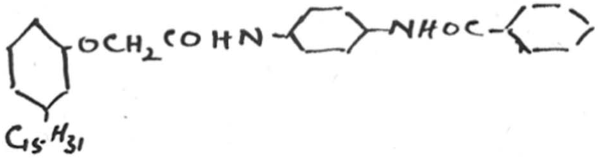
and (XIII) by reducing (XII)



Check
Fast Base

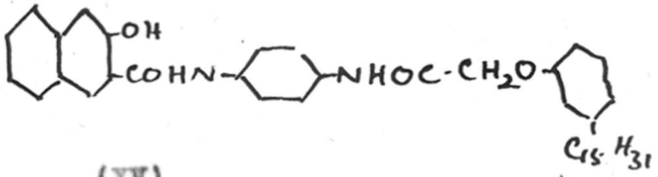
(XIII)

and (XIV) by benzoylating (XIII)



(XIV)

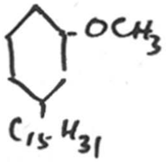
and (XV) by condensing(XIII) with β-hydroxynaphthoyl chloride to obtain (XV)



(XV)

✓

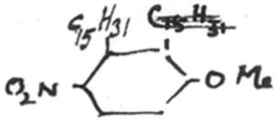
Tetrahydroanacardol has been methylated to produce (XVII)



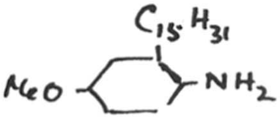
Phth - anh.

(XVII)

and attempts are being made to nitrate it to produce



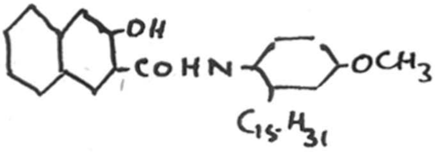
which on reduction will give the amine



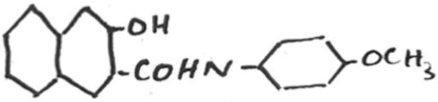
?

and this could be condensed with β-hydroxynaphthoyl chloride to yield

Has this been done?



Such a naphthol would resemble the commercial Naphtol AS-RL



with the exception of the alkyl chain, the latter giving it the added advantage of excellent rubbing fastness.

Examination of the dyeing properties of the various compounds synthesised are under progress.

EXPERIMENTAL

Preparations of cashew nut shell oil described in literature are tedious and time consuming. The roasting method of oil extraction led to partial polymerisation of the oil and decarboxylation of the anacardic acid present. Gandhi (Ph.D. Thesis, Bombay Univ.) adopted a dual method of expression in a hydraulic cement testing apparatus and extraction of the residual shells in lignin, in a Soxhlet. The yield by this method was 30.4% on the weight of the shells.

Two new methods have now been developed for the preparation of the oil. In the first case, cashew nut shells cut into small bits (100 g.) were shaken with alcohol (400 c.c.) at room temperature (30°C.), and left overnight. The alcohol was decanted off and the residue in the vessel treated again twice using alcohol (300 c.c.) each time, the duration of treatment in the latter case being 30 minutes. It was noticed that, while the first and second extractions gave fairly deeply coloured solutions, the third was coloured a pale brown. The extracts obtained from all the three ~~six~~ cases were mixed, filtered and the oil collected by distilling off the alcohol under vacuum. The yield by this method was 32%.

Since the above method involved application of heat with resultant polymerisation of a portion of the oil, an attempt was made to confine the extraction and collection of the oil to room temperature (30°C.). The crushed shells (480 g.) were treated as in the previous case with alcohol (900 c.c.) and filtered. The filtrate was shaken with common salt solution (5%) in a separating funnel to effect the removal of alcohol, salt being added to avoid emulsification and consequent loss in yield of oil which would result, if water alone were added. The lower layer removed and the alcohol recovered by distillation. The upper layer was filtered through asbestos and dried in a desiccator under vacuo. The yield by this method was 38%.

According to Ruhemann and Skinner (*Ber.*, 1887, *20*, 1861) and Sudborough (*J. Ind. Inst. Sci.*, 1923, *5*, 133; *Chem. Abs.*, 1923, *17*, 1897) the oil contains anacardic acid and "cardol" which is probably a mixture of phenolic and other components. Pillay (*J. Ind. Chem. Soc.*, 1935, *12*, 226) found that cashew nut shell oil contained anacardic acid to the extent of 90%. In view of this fact and since the value of an oil would mainly depend on its anacardic acid content, it seemed of interest to examine the oil extracted by the above methods, a sample obtained by pressing, the oil extracted from the residual shells after pressing and samples of oils received from a few reputed dealers for their anacardic acid contents and iodine value; the former was determined by direct titration of the oil dissolved in aqueous alcoholic solution and the latter by Wij's method. A new rapid method for determination of iodine value suggested by Jasperson (*J. Soc. Chem. Ind.*, 1942, *61*, 115) did not give satisfactory results as the end point could not be detected with any degree of certainty. The results are recorded in Table I.

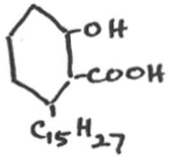
Table I/

Table I

	Sample	Colour	Iodine value	Anacardic acid present
I	Extracted with alcohol	Reddish brown	175.6	43.0
II	Obtained by pressing	Deep red brown	183.2	57.5
III	Obtained from shells from II by alcohol extraction	Pale red brown	171.3	50.0
IV	Hot pressed	Dark brown	185.8	2.8
V	A	Chocolate brown	218.4	7.0
VI	B	Olive brown	134.3	8.5
VII	C	Blackish brown	176.0	60.0
VIII	D	"	176.2	58.1

Since none of the oils analysed exhibited any tendency to behave as drying oils in spite of their high iodine value, the values appeared inexplicable. The explanation probably lies, as indicated by Gardner (Circ. U. S. Paint Manufacturers' Association, 1923, 180, 241; Chem. Abs., 1923, 17, 2512), in the anti-catalytic action of the phenolic constituents. The high iodine value may also be explained by nuclear absorption.

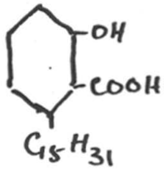
Preparation of anacardic acid:



Cashew nut shell oil, obtained by cold extraction (50 g.) was dissolved in hot alcohol, and to this was added lead hydroxide slurry in alcohol. (The lead hydroxide being obtained by adding liquor ammonia (17 c.c.) to an aqueous solution of lead nitrate (15 g.) and stirring mechanically). The lead hydroxide which separated was collected by decanting off the supernatant liquid, washed with water to free from ammonia and made into a slurry with alcohol. The pale brick red lead anacardate that settled down was washed with alcohol to free it from "cardol" and other impurities and the washings so obtained, were again treated with lead hydroxide slurry in the same manner as before to collect any anacardic acid that may have been washed out. The lead salt was treated with acetic acid and extracted with ether, the extract washed with water to remove last traces of lead and the oil (20 g.) recovered by distilling off the ether (cf. Pillay, loc. cit.).

A slight modification in the above procedure was found to be desirable in view of the emulsification that was taking place during the course of washing the anacardic acid to free from lead. The emulsion that formed had either to be broken up with a solution of common salt or an unduly large quantity of ether had to be used up. To eliminate this, dilute hydrochloric acid was tried in place of acetic acid with success. The lead chloride was easily washed out, and in the absence of emulsification with inevitable loss in the acid content in the course of the washing out operation, an increase in yield to the extent of 3% was observed.

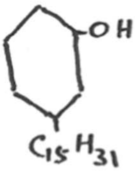
Preparation of tetrahydroanacardic acid:



A Anacardic acid (10 g.) in alcohol (50 c.c.) was hydrogenated for 3 hours using Adams platinum oxide catalyst in the Parr Hydrogenation Apparatus, the alcoholic solution filtered off and the tetrahydroanacardic acid recovered by distilling off the alcohol.

It was crystallised (Norit) from benzene. It melted at 92°C. (cf. Pillay, *loc. cit.*).

Preparation of tetrahydroanacardol:



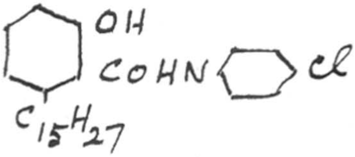
The tetrahydroanacardol (15 g.) was obtained by hydrogenation of anacardol (20 g.), the latter being obtained by distillation of cashew nut shell oil. It proved more difficult to crystallise than the tetrahydroanacardic acid and was finally crystallised from ligroin. It melted at 54-55°C. (cf. Pillay, *loc. cit.*).

Preparation of the arylides of anacardic and tetrahydroanacardic acids: The preparation of the arylides of anacardic and tetrahydroanacardic acids proved more difficult than at first anticipated. The method adopted by Gandhi (*loc. cit.*), in which phosphorus trichloride was used as the condensing agent the acid and the base being kept in solution by pyridine, was tried. In this case, anacardic acid (5 g.) (1 mol.) dissolved in pyridine (15 c.c.) was taken in a three necked flask and to this was added p-chloraniline (2 g.) (1.1 mol.) also dissolved in the same solvent. The temperature was raised to 60°C. and phosphorus trichloride (2 g.) was added from a dropping funnel slowly in the course of 30 minutes. After the addition was complete the temperature was maintained at 60°C. for a further period of 30 minutes and then raised to 120°C., and the heating continued at this temperature for 1 hour. The reaction product was poured over ice and hydrochloric acid when an oily substance was found to be formed. This was taken in ether and washed with hydrochloric acid till free from pyridine, washed with water till free from acid (Congo), and dried over anhydrous sodium sulphate, the ether distilled off and the viscous oily product (4.6 g.) collected.

To test if the condensation had taken place at the carboxyl, a simple titration against caustic soda was made, phenolphthalein being used as the indicator. The substance (0.11 g.) was dissolved in neutral alcohol (20 c.c.) and this further diluted by addition of distilled water (15 c.c.) and titrated against 0.115 N caustic soda, of which 2.7 c.c. were required, corresponding to a molecular weight of 354.8 indicating that the carboxyl was free.

The ortho hydroxy carboxylic structure of anacardic acid suggested the employment of similar methods as in the case of β-hydroxynaphthoic acid being tried for the preparation of the acid chloride (cf. Bhat, Forster and Venkataraman, J. Soc. Dyers Col., 1940, 56, 166). In this method anacardic acid dissolved in petroleum ether, b.p. 60-70°, was refluxed with an excess of thionyl chloride on a water bath maintaining the temperature at 70-80°, the excess thionyl chloride being distilled off under reduced pressure. The acid chloride thus obtained was used for the condensations.

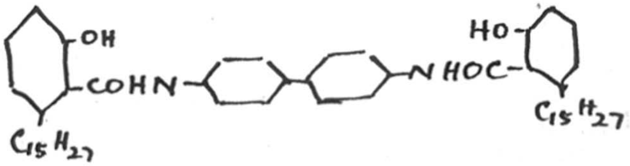
Anacardyl-p-chloranilide (I):



Anacardic acid (5 g.) was dissolved in petroleum ether b.p. 60-70° (20 c.c.), thionyl chloride (5 c.c.) added and refluxed for 1 hour over a water bath, maintaining the temperature of the bath between 70-80°C., the thionyl chloride removed under vacuum. The viscous brown reaction product was dissolved in dioxan (20 c.c.) and to this was added p-chloraniline (2 g.) also dissolved in the same solvent. The contents refluxed for 1 hour. On pouring into water, a brownish sticky product separated, which was washed with water to remove dioxan and with hydrochloric acid to remove any unreacted amine, washed and dried. The sticky product obtained (3.4 g.) was found to give no titre against decinormal caustic soda indicating the absence of free carboxyl group. Attempts at diazotisation to test for the existence of any free amine also gave negative results (Found Cl, 8.0. $C_{28}H_{36}O_2NCl$ requires Cl, 7.8%). It gave a blue colouration with ferric chloride.

Sample N7D

Dianacardyl benzidide (II):



(II)

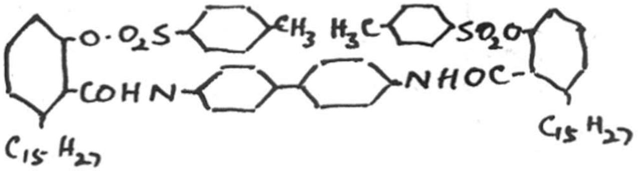
Anacardyl chloride (6 g.) prepared as above was dissolved in dioxan (30 c.c.) and to this was added benzidine (1.8 g.) dissolved in the same solvent. At

Samples

first an olive green product was formed which, on refluxing, changed to yellow brown. The sticky product (4.2 g.) obtained on pouring into water was taken in ether and washed repeatedly with dilute hydrochloric acid and then with water till free from acid, the ether distilled off and the substance dried in a desiccator. The product thus obtained was semi-solid. It was analysed for nitrogen content by Dumas method. (Found: N, 3.7. $C_{56}H_{72}O_4N_2$ requires N, 3.4%). It was coloured yellowish green with ferric chloride.

m-p-?

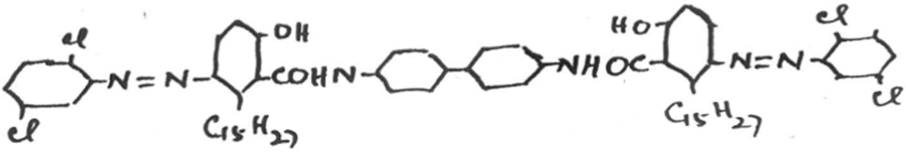
Dianacardylbenzidide-p-toluenesulphonate (III):



(III)

To dianacardylbenzidide (2 g.) in dry distilled pyridine (20 c.c.) was added p-toluenesulphonyl chloride (3.1 g.) and refluxed for 2 hours and left overnight. The brown coloured product obtained on pouring into crushed ice and hydrochloric acid, could not be crystallised. It was repeatedly washed with dilute ~~wake~~ hydrochloric acid to free from pyridine, washed with water and dried. (Found: S, 5.0. $C_{70}H_{84}O_8N_2S_2$ requires S, 5.6%).

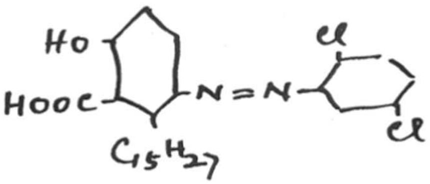
Bis-5-(2':5'-dichchlor)benzeneazo-dianacardyl benzidide (IV):



(IV)

2:5-Dichloraniline (0.84 g.) was diazotised by stirring up in hydrochloric acid 32% (1.8 c.c.) mixed with water (10 c.c.) and to this was added sodium nitrite (0.4 g.) dissolved in water (15 c.c.), the temperature during diazotisation being maintained at 10°C. the excess mineral acidity was neutralised (Congo) by addition of sodium acetate (2.2.g.). The diazo solution was added slowly into dianacardyl benzidide (2 g.) dissolved in alcohol (10 c.c.) containing caustic soda (32.5%, 1.5 c.c.) and water (20 c.c.). The brownish product (2.4 g.) crystallised from acetylenetetrachloride in brown coloured needles, which did not melt below 300°C. (Found: Cl, 11.6. $C_{68}H_{78}O_4N_6Cl_4$ requires Cl, 11.9%).

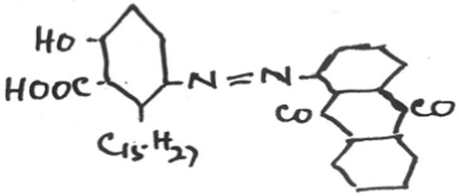
5-(2':5'-Dichloro)benzeneazoanacardic acid(V):



(V)

Anacardic acid (5 g.) was dissolved in alcohol (20 c.c.) and to this was added water (20 c.c.) and caustic soda (32.5%)(2.0 c.c.). Into this was poured in thin stream 2:5-dichloraniline (2.6 g.) diazotised in the usual manner. The resultant oily dye, which was orange red in colour was taken up in ether and washed with water and then with dilute sodium carbonate and again with water till the wash water was no longer coloured. The ethereal extract dried over anhydrous sodium sulphate. The ether was removed by distillation and a dark reddish brown product (3.4 g.) obtained. (Found: Cl, 13.2. $C_{28}H_{34}O_3N_2Cl_4$ requires Cl, 13.7%).

5-α-Anthraquinoneazoanacardic acid (VI):



(VI)

Diazotisation of α-aminoanthraquinone was carried out by the special method indicated by Hodgson (*J. Chem. Soc.*, 1933, 1620) as the usual methods involving the use of hydrochloric acid and sodium nitrite did not lead to the formation of the diazo compound. In the new method, α-aminoanthraquinone (2 g.) was dissolved in boiling glacial acetic acid (24 c.c.) and cooled down to room temperature (30°C.). This was gradually added to sodium nitrite (1 g.) in sulphuric acid 98% (7 c.c.). During diazotisation, the temperature was maintained at 20°C. The sodium nitrite in sulphuric acid was prepared by adding finely powdered sodium nitrite to the previously cooled acid with vigorous stirring, the temperature raised to 70° till the nitrite had dissolved, and the solution cooled. Coupling was effected by dissolving anacardic acid (3 g.) in alcohol (10 c.c.) to which was added water (20 c.c.) containing caustic soda 32.5% (1.2 c c.). This resulted in a clear solution. Into this solution was led in a thin stream, α-aminoanthraquinone (2 g.) diazotised as above. The bright red coloured dye (3.6 g.) obtained, crystallised from alcohol in fine needles melting at 138-40°C. (Found: N, 4.7. $C_{36}H_{38}O_5N_2$ requires N, 4.9%). This gave a reddish orange colour with sulphamic acid and golden orange with nitric acid.

Calphamate
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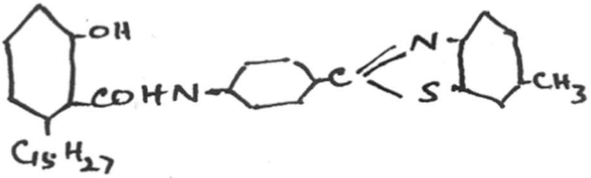
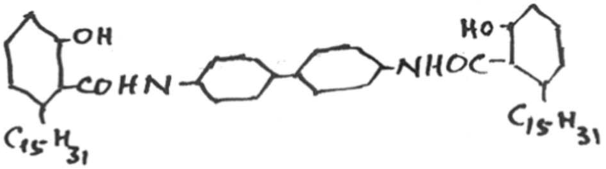
Anacardyl dihydrothiotoluidide (VII):



(VII)

To anacardic acid (5 g.) was added petroleum ether, b.p. 60-70° (25 c.c.) and thionylchloride (5 c.c.) and processed with usual manner. To the acid chloride thus obtained was added dioxan (50 c.c.) and dehydrothiotoluidide (3.8 g.) also dissolved in the same solvent and refluxed for 1 hour. The reaction product was poured into water and the sticky yellow brown product washed repeatedly with water to remove all dioxan. It was shaken up with ether and the pale brown coloured ethereal layer removed. The brown coloured insoluble product (6.3 g.) obtained after ether treatment, was treated with dilute hydrochloric acid and washed with water till free from acid. It could not be crystallised (Found: S, 5.8. $C_{36}H_{42}O_2N_2S$ requires, S, 5.6%).

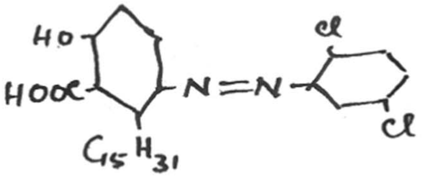
Di-tetrahydroanacardyl benzidide (VIII):



(VIII)

The procedure adopted in this case was the same as in the case of the di-anacardyl benzidide. The yield obtained was slightly more as starting with tetrahydroanacardic acid chloride (2 g.) and benzidine (0.7 g.) a yield of (2.3 g.) was obtained, the isolation of the reaction product ~~was~~ presenting no difficulty. Crystallisation was effected from benzene, the pale brown plates melted at 139-41°. (Found: N, 3.4. $C_{56}H_{80}O_4N_2$ requires N, 3.4%).

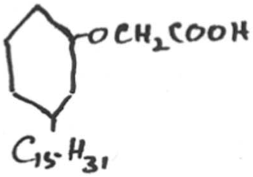
5-(2':5'-Dichloro)benzeneazotetrahydroanacardic acid (IX):



(IX)

Tetrahydroanacardic acid (3 g.) dissolved in alcohol (10 c.c.) and water (30 c.c.) containing caustic soda (32.5%; 1.2 c.c.), was coupled with diazotised 2:5-dichloraniline (1.5 g.) in the usual manner. The resultant dye crystallised from a mixture of alcohol and acetic acid in clustres of brown needles melting at 112-14° (Found: Cl, 14.0. $C_{28}H_{38}O_3N_2Cl_2$ requires Cl, 13.6%).

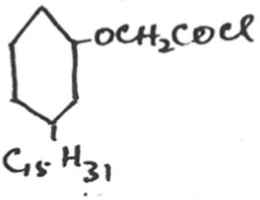
m-Pentadecylphenoxyacetic acid (X):



(X)

Monochloracetic acid (6 g.) in alcohol, was added to tetrahydroanacardol (5 g.) dissolved in alcohol (30 c.c.) containing caustic soda (32.5%; 18 c.c.), and the mixture refluxed on a water bath for 3 hours. The alcohol was distilled off, the contents diluted with water made acidic with hydrochloric acid and extracted with ether. The ether extract was next washed with water till free from acid and then treated with dilute sodium carbonate solution. The sodium salt of the acid thrown out of ether was collected and washed repeatedly with ether to free from tetrahydroanacardol. The sodium salt was suspended in water and acidified with hydrochloric acid and warmed gently to remove ether. The free acid thus precipitated was washed with water to remove mineral acidity and crystallised from alcohol. Colourless flat needles (3.8 g.) melting at 103-104°C. were obtained.

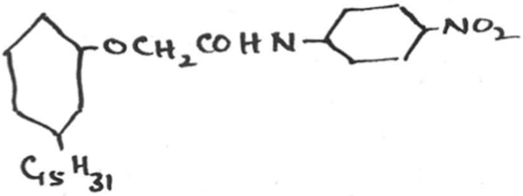
m-Pentadecylphenoxyacetyl chloride (XI):



(XI)

m-Pentadecylphenoxyacetic acid (3.5 g.) was heated with thionyl chloride (15 c.c.) over a water bath for 3 hours, the excess thionyl chloride removed by distillation and the m-pentadecylphenoxyacetyl chloride used directly for condensation with p-nitraniline.

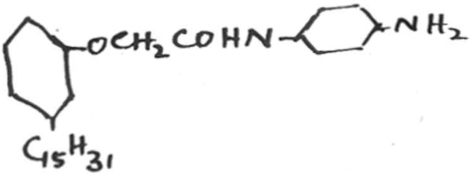
m-Pendadecylphenoxyacetyl-p-nitranilide (XII):



(XII)

p-Nitraniline (1.4 g.) dissolved in dry pyridine (15 c.c.) was refluxed for 2 hours with m-pentadecylphenoxyacetyl chloride (3.5 g.) also dissolved in the same solvent and left overnight. The reaction product was poured into ice and hydrochloric acid, washed with water and dried. It crystallised from alcohol in pale cream coloured plates melting at 88-89°C. (Found: N, 5.6. $C_{29}H_{42}O_4N_2$ requires N, 5.8%).

Mono-N-(m-pentadecylphenoxy)acetyl-p-phenylenediamine (XIII):

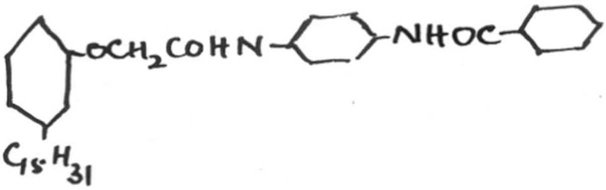


(XIII)

m-Pentadecylphenoxyacetyl-*p*-nitranilide (4 g.) was taken in a flask (250 c.c.) and into this were added iron filings (4 g.) hot water (150 c.c.) and glacial acetic acid (10 c.c.) and the contents refluxed for 3 hours.

In the beginning considerable amount of frothing took place and the contents had to be shaken up vigorously and the flame lowered to ~~mm~~ minimise this effect. After about 30 minutes the frothing subsided and the reduction went on smoothly. At the end of the period the supernatant aqueous extract filtered off and concentrated and the sludge remaining in the flask extracted thrice with absolute alcohol, using (50 c.c.) each time. These extracts mixed with the aqueous one. Since only a small amount of the amine separated out, hot water was added and the product collected and crystallised from acetic acid in pale cream coloured plates (2.8 g.). It did not give a sharp melting point softening at 80°C., it became more mobile at 110°C. and remained practically in this condition below 300°C. (Found: N, 5.8. $C_{29}H_{44}O_2N_2$ requires N, 6.1%).

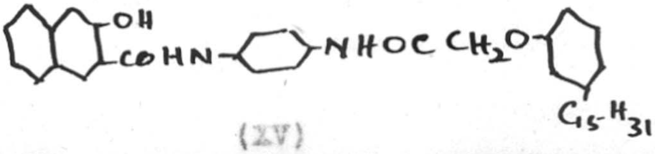
N-(*m*-Pentadecylphenoxy)acetyl-N'-benzoyl-*p*-phenylenediamine (XIV):



(XIV)

m-Pentadecylphenoxyacetyl-*p*-phenylenediamine (1 g.) in pyridine (10 c.c.) was shaken up with benzoyl chloride (0.6 g.). The reaction product poured into ice and hydrochloric acid, collected and crystallised from acetic acid in colourless plates which did not melt below 300°C. (Found: N, 4.4. $C_{36}H_{48}O_3N_2$ requires N, 5.0%).

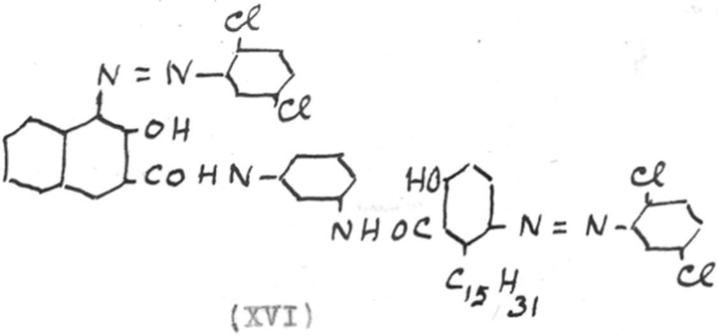
N-2-Hydroxy-3-naphthoyl-N'-*m*-pentadecylphenoxyacetyl-*p*-phenylenediamine (XV):



(XV)

2-Hydroxy-3-naphthoyl chloride (0.9 g.) was dissolved in solvent naphtha (20 c.c.) to which m-pentadecylphenoxyacetyl-p-phenylenediamine (2 g.) also dissolved in the same solvent, added and the mixture refluxed over an oil bath at 150°C. for 2 hours. On cooling a waxy pale brown product separated which was washed with petroleum ether and dissolved in caustic soda and alcohol, filtered and the filtrate treated with dilute hydrochloric acid to precipitate the naphthol formed. It was washed free from acid. It could not be crystallised and did not melt below 300°C. (Found: N, 3.9. $C_{40}H_{50}O_4N_2$ requires N, 4.5%).

Dye from N-2-hydroxy-3-naphthoyl-N'-tetrahydroanacardyl-m-phenylenediamine and 2:5-dichloroaniline(XVI):

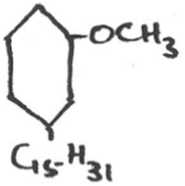


(XVI)

N-2-Hydroxy-3-naphthoyl-N'-tetrahydroanacardyl-m-phenylenediamine (cf. Part I, this Thesis)(0.2 g.) dissolved by addition of alcohol (5 c.c.) and water

(20 c.c.) containing caustic soda (32.5%; 0.75 c.c.) was coupled with 2:5-dichloraniline (0.12 g.) diazotised in the usual manner. The yellow brown dye (0.15 g.) crystallised from a mixture of alcohol and acetic acid in plates which did not melt below 300°C. (Found: Cl, 15.6. $C_{51}H_{48}O_4N_6Cl_4$ requires Cl, 14.9%).

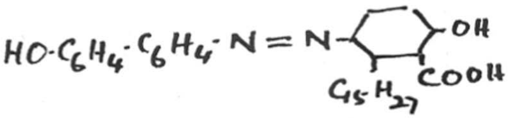
Tetrahydroanacardol methyl ether (XVII):



(XVII)

Tetrahydroanacardol (5 g.) (1 mol.) dissolved in acetone (20 c.c.) and neutralised with caustic soda (10% solution) till alkaline to phenolphthalein. To this dimethyl sulphate (10.4 g.) (5 mols.) was added gradually keeping the mixture alkaline throughout the addition with caustic soda 50% solution. The acetone was driven off and the product heated over a water bath for 1 hour. The heavy oil that settled down was ether extracted and ~~this~~ washed with water till free from caustic soda. The extract was then dried over anhydrous sodium sulphate, the ether evaporated off and a heavy pale yellow coloured oil (4 g.)was obtained. (Found: H, 11.7. $C_{22}H_{38}O$ requires H, 11.9%).

5-p-Hydroxydiphenylazoanacardic acid(XVIII):



(XVIII)

Benzidine (1.6 g.) (1 mol.) was diazotised and coupled with anacardic acid (3 g.) (1 mol.) dissolved by addition of alcohol (10 c.c.) and water (40 c.c.) containing caustic soda (32.5%; 2 c.c.). After 15 minutes, the mixture boiled for 2 hours, the product that settled down extracted with hot glacial acetic acid from which the dye crystallised out in fine yellow brown needles (1.7 g.). (Found: N, 5.5. $C_{34}H_{40}O_4N_2$ requires N, 5.2%).

Part III

Coupling of cutch with diazo salts.

INTRODUCTION

As a cottage industry, particularly in India, many natural organic colouring matters are still finding limited employment for dyeing purposes; some, e.g. Kamala, are used for medicinal purposes on account of their real or fancied pharmacological properties. So far as dyeing in the mill is concerned, the majority of the natural colouring matters have been replaced by coal-tar dyes owing to their advantages in regard to the brilliancy and range of shades, fastness properties, simplicity of application and the standard quality of the marketed product. Nevertheless, a few natural dyes have survived and their continued use is not so much in the countries of their origin as in those where the technical side of the cotton industry is most highly developed. In India, no cotton mill handles a vegetable dye. The two main reasons why a few plant colouring matters are used in large scale dyeing and printing elsewhere are their cheapness in producing deep shades, and the peculiar mellowness of of the tints which may be difficult to match with synthetic dyes.

The use of natural Indigo is restricted to the fulfilment of special orders, e.g. certain army contracts, in which a blue produced from natural Indigo on a Sanderswood bottom is specifically mentioned. With the exception of Indigo, all vegetable dyes in use are mordant dyes. Incidentally, all are phenolic substances to which the after-treatment for cutch described in the present thesis would apply, but experiments with a few polyhydroxyflavones have shown that there is no improvement in the shades or the fastness properties. The most extensively used of the plant colouring matters is probably Logwood, mainly on wool and silk and in conjunction with other dyes; thus Logwood Black on chrome mordanted wool is bluish in tone and a 'deal' black is obtained by adding 2-5% of Old Fustic. On cotton the direct and sulphur blacks, with their advantage of substantivity, are simpler and cheaper to apply, but Logwood is still valuable for topping purposes. In addition to its use in admixture with Logwood for shading purposes, Old Fustic, the wood of the Chlorophora tinctoria , gives a bright yellow, fast to light, soaping and milling, on chrome-mordanted wool. Both for shading with Logwood and for dyeing wool by itself on aluminium, chromium, iron and tin mordants, Quercitron Bark finds limited application. Flavine and Cochineal are used together for the production of scarlets and oranges on wool. The last, and in many ways the most important example, is Catechu or Cutch which is the subject of this thesis.

In calico printing also, the plant colouring matters mentioned, to which may be added Persian Berries, appear to be still employed to some extent in Europe. Logwood Black is adaptable to a wider variety of purposes than synthetic blacks (Fothergill, "Principles and Practice of Textile Printing", 1936, pp. 301, 305) and it therefore plays "an important part in the production of black-ground steam styles". Persian Berries are largely used in printing for producing steam yellows, browns, oranges and olives, using aluminium, chromium and tin mordants, and combinations of these. Quercitron Bark is applied in an analogous manner, the shades obtained being yellower and not quite so bright; in producing olives and browns, the bark extract may be used in conjunction with the Alizarin dyes and basic dyes, which form insoluble complexes with the phenolic ketones constituting the natural mordant dyes and which therefore do not require in this case the use of tannin or Katanol mordants.

Whilst numerous varieties of cutch are employed by dyers and tanners, Bengal cutch (Brown cutch, Pegu cutch, Kath, Katha, Koir, Khaira, Kuti), the extract prepared from the wood of "Khair" trees (acacia catechu) which are found all over India and Burma, represents the commonest variety of cutch on the Indian market. The trees are felled when full of sap; the red heartwood is then chopped up to small sticks and extracted with boiling water. Concentration of the liquor leads to cutch, graded according to the colour, dyeing and tanning properties. The older village methods of preparation, and the modern process involving the use of steam mills and vacuum pans, as practised by Indian Wood Products Ltd. at Izzatnagar, United Provinces, are described in detail by Sen-Gupta ("Manufacture of Catechu", Industry Publishers, Calcutta, p. 1). Three products are marketed; dark cutch, pale cutch and Kheersal. After extracting the wood in autoclaves, the aqueous liquor is concentrated in vacuum pans. The crystalline material that separates on cooling and allowing to stand is collected on a centrifuge;* when dried at 100°C. the product is pale cutch or katha, which finds a large sale in India for chewing with "pan". The mother liquor is concentrated to about 15°Tw. in triple effect evaporators; on further drying in the open, dark cutch is obtained and exported for use in dyeing sails, fishing nets and canvas. Kheersal is not separated in the ordinary factory process for the manufacture of cutch and katha; it is stated to be practically pure crystalline catechin and may be separated mechanically from the wood in which it is occasionally found embedded. Both katha and Kheersal are alleged to have pharmacological and medicinal properties.

In view of the wide occurrence of cutch-containing trees in India, it seemed of interest to re-examine the dyeing properties of cutch. Hummel and Brown (<u>J. Soc. Dyers Col.</u>, 1896, <u>12</u>, 224) divide Indian cutches into three groups according to (a) the colour produced by the cutch-copper sulphate bath and (b) by after-chroming. Thus (I) pale yellowish-brown ⟶ not materially darkened; (II) reddish- or orange-brown ⟶ redder and darker; and (III) pale yellowish-cinnamon ⟶ reddened. The ordinary methods of applying cutch to cotton, wool and silk in dyeing and printing are well established; the main objective of the present work has been to devise a process for after-treating the dyed materials by which without materially impairing the excellent fastness properties of cutch dyeings, a larger variety of shades than the usual browns may become available. The use of catechu is now restricted to the well known Catechu Brown or Cutch Brown on cotton and to weighting purposes in silk dyeing. In dyeing cotton the material is steeped in a boiling solution of Cutch to which an addition of copper sulphate has been made. Cutch has little or no substantivity towards the cotton fibre. After working in the cooling bath for 1 hour or more, the material is transferred without washing, but after hydroextraction if desired, to a second or developing bath containing sodium bichromate. During this process of oxidation, as in the case of tanning, it appears probable that catechin is first converted into catechutannic acid, the latter then undergoing a further change by oxidation to an insoluble brown substance, which is firmly fixed on the fibre. According to Hummel and Brown (loc. cit.) catechin with copper sulphate gives the same shade as catechutannic acid without this addition; by the use of copper sulphate in the second case still deeper shades are obtained. It should be noted, however, that catechin being a 5-hydroxypyran, it is conceivable that oxidation involves the formation of a γ-pyrone, which would then be capable of forming a copper or chromium lake, chelation of the pyrone oxygen with the chromium in the 5-position becoming possible. Although this view of dyeing with cutch involves also the intermediate formation of catechutannic acid, it is doubtful if the tinctorial power of a given sample of cutch would bear a linear relationship to the content of catechutannic acid. For one thing, the latter is more soluble in water and, as far as preliminary experiments in this direction indicate, it is also less substantive to cotton than catechin.

Catechu may be dyed in admixture with direct dyes, chosen with regard to their ability to withstand the action of copper sulphate and bichromate, the process being cheaper than topping with basic dyes (Falke, *Farben Ztg.*, 189 1894, No. 22; *J. Soc. Dyers Co.*, 1894, *10*, 190). An addition of common salt or Glauber's salt may be made for exhaustion.

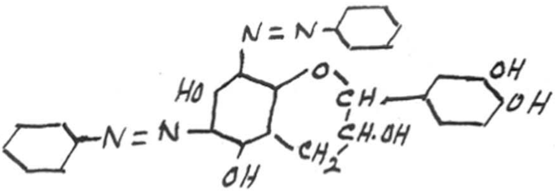
Basic dyes may be dyed on a catechu bottom; the catechu acts as a mordant, the dye forming with it an insoluble lake, and other mordanting is unnecessary.

At the present day cutch is probably used to a large extent in printing than in dyeing (Fothergill, *loc. cit.*). The two main classes of printing in which it finds employment are in producing "steam browns and drabs, very fast to soap, light, acids and alkalis, and in the Madder dyed style for producing browns in combination with red, chocolate and purple". As in the case of the other and more modern mordant dyes, chromium acetate is almost exclusively employed. The cutch may be printed on with a starch-tragacanth or British gum thickening, using chromium acetate as mordant and sodium chlorate as oxidising agent. Prolonged ageing in the steaming cottage without pressure is preferable to ageing in the Mather and Platt Rapid Ager. A final fixation in hot sodium bichromate solution may be effected.

Cutch dyeings on wool are only moderately fast to light, but very fast to scouring and milling. On cotton, the use of copper sulphate in the bath, as in the case of some of the direct dyes which are after-treated with copper salts, greatly improves the fastness to light; the chroming improves the fastness to washing. Catechu brown dyed by the standard method employing copper sulphate and bichromate is reputed to be very fast to light, soaping, bleaching and salt water. To quote A. G. Perkin (Thorpe's Dictionary of Applied Chemistry, 1927, 11, 105), it is exceedingly fast to light, acid and alkaline solutions, and also to bleaching powder. Huebner("Bleaching and Dyeing of Vegetable Fibrous Materials", 1920, p. 179) recommended catechu as being specially suited for heavy brown shades which are remarkable for their fastness. Its use in the dyeing of ship's sails is said to be based on its excellent fastness properties and on its preservative action, preventing sea-water from rotting cotton. The fastness to light is somewhat exaggerated; in deep shades the fastness would correspond to grade 6 and in medium shades it is grade 5. According to Nelson (Amer. Dyestuff Rep., 1924, 13, 597; see also Holtkapp, ibid., 1935, 24, 389; Durant, Dyer, 1937, 77, 335, 389, 441), not only do cutch dyeings exhibit greater fastness to weather conditions than do dyeings with coal tar dyes, but they are also less liable to attack by mildew. This would support the earlier statement of Nanson(Text. Amer., 1913, 19, 17) that fabrics, which have to withstand prolonged exposure to the weather and are used under conditions favourable to the growth of mildew, are best dyed with catechu. The treatment of jute for rot-proofing with cutch and potassium bichromate, so that an insoluble chromium complex is deposited on the fibres to the extent of about 2% on the weight of the material, has recently been patented (Lowry, B.P.

462,306). Renard and Serol (Rev. Gen. Tein. Imp. Blanch. App., 1935, 13, 781), who have given a detailed account of dyeing methods, consider that cutch dyeings are much more stable and cheaper than dyeings with sulphur dyes.

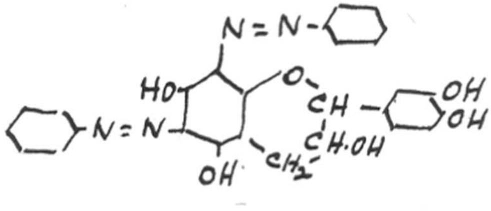
The more important natural colouring matters of the flavone, flavonol and pyran groups, including those which have survived the advent of synthetic dyes for use in dyeing and printing, contain the phloroglucinol nucleus and are therefore capable of coupling with diazo salts. As early as 1876, Weselsky (Ber., 1876, 9, 217) prepared the diazobenzene derivative of cutch. A. G. Perkin (J. Chem. Soc., 1896, 69, 1439; 1898, 73, 666, 1028) utilised this reaction for characterising a number of phenolic colouring matters, e.g. chrysin, apigenin and euxanthrone. In the case of catechin itself, A. G. Perkin and Yoshitake (J. Chem. Soc., 1902, 81, 1162) prepared disazobenzene-catechin in substance by treating an aqueous solution with diazobenzene sulphate



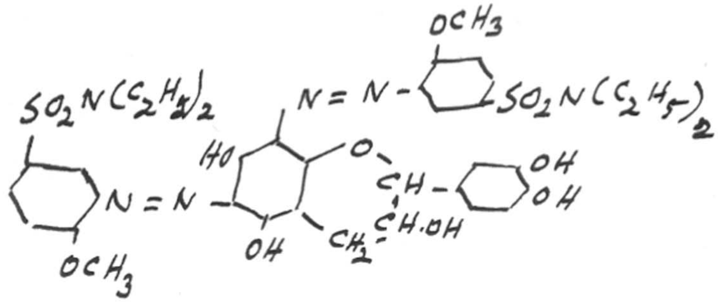
The reaction has also been found useful for identifying some of the isomeric catechins which form disazobenzene derivatives with characteristic melting points.

Thompson and Claus (<u>B.P.</u> 14,836 of 1888; <u>J. Soc. Dyers Col.</u>, 1889, <u>5</u>, 149) patented the preparation of colouring matters from cutch, Logwood and Quercitron Bark by the action of diazocompounds, several of the products being useful in dyeing and printing. Dyes were also obtained by coupling tetrazotised benzidine, its homologues and disulphonic acid with 1 mol. cutch and then with 1 mol. of a phenol or naphthol. These products dyed wool from a weak acid bath and could also be used for dyeing and printing calico in conjunction with chromium, aluminium and iron mordants; in printing they were claimed to be valuable steam colours. The tetrazodiphenyl derivatives were rather insoluble. The amines specifically mentioned in this patent were aniline, toluidine, xylidine, α- and β-naphthylamine, sulphanilic acid, <u>m</u>-phenylenediamine, <u>p</u>-aminoazobenzene and its mono- and disulphonic acids, benzidine, tolidine and benzidine disulphonic acid. No attempt was made, however, to investigate the utility of the process for altering the~~s~~ shades and improving the fastness of cutch dyeings. The only reference in the literature to the possibility of after-treating cutch-dyed material with a diazo salt is the treatment of cotton dyed with Pegu cutch with diazotised p-nitraniline, a rde redder and about 1% lighter shade being obtained (Weingartner, Österreichs Wollen u. Leinen Industrie, 1903, **19**, 76; J. Soc. Dyers Col., 1903, **19**, 73). Since the stabilised diazo salts and their wide application on Naphtol AS grounds are much more recent, the coupling of diazobenzene chloride with catechin has not hitherto been extended practically to coupling a range of more complex diazonium salts with cutch on the cotton fibre. With the exception of those containing sulphonic groups, azo dyes produced from cutch in substance (such as those described in the patent of Thompson and Claus) are more or less insoluble in water and therefore not capable of direct application to cotton. Further, a normal cutch dyeing from a copper sulphate bath and after-treated with bichromate exhibits little activity towards diazo salts. The change to japonic acid, or to any other substance which constitutes Catechu Brown, undoubtedly involves the loss of hydroxyl groups by anhydride formation and by conversion to quinonoid forms; in any case the difference in the behaviour of pure catechin in a freshly prepared solution and of Catechu Brown towards diazonium chlorides is* marked. Cutch dyeings have now been treated with a series of diaz salts from the Fast Bases, leading to a range of bright and attractive shades (Ind. P. 24,056). The application of cutch by padding processes, in which, in addition to the obvious economy in time, the oxidation of catechin which hinders coupling with diazo salts is obviated, has also been studied. One of the causes for the partial or complete abandonment of natural mordant dyes is the tediousness of the dyeing methods; this is especially true of the recognised process for Catechu Brown, which require several hours for completion. In order to obtain full shades from cutch by the normal methods, increasing the concentration of the bath is inadequate and "building up" by repeated treatment is necessary (Hummel and Brown, loc. cit.).

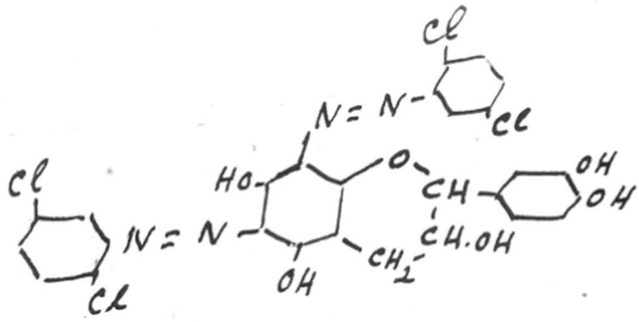
The coupling reaction of Perkin and Yoshitake (loc. cit.) has now been extended to cover besides aniline, a wider range of amines, such as o-anisidine-5-sulphondiethy amide, 2:5-dichloraniline and 4-chloro-2-aminotoluidine to yield compounds (I), (III), (V) and (VII) respectively


N = N -
HO
N = N
O
CH
CH.OH
CH2
OH
OH
OH

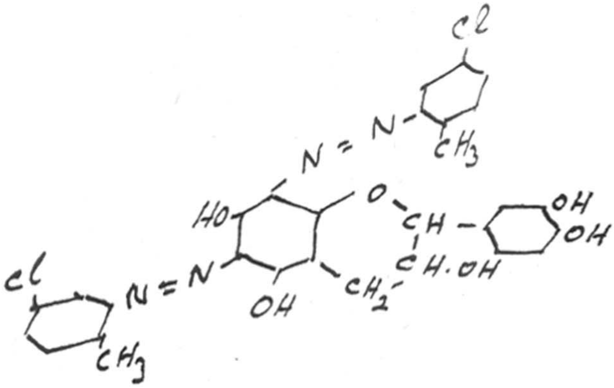
(I)


OCH3
SO2N(C2H5)2
N = N -
SO2N(C2H5)2
HO
N = N
O
CH
OH
OH
CH.OH
CH2
OH
OCH3

(III)

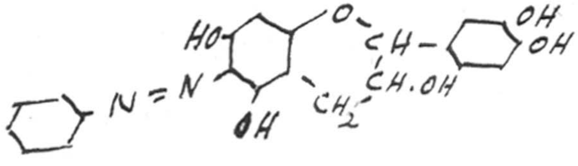

Cl
N = N -
Cl
Cl
HO
N = N
O
CH
OH
OH
CH.OH
CH2
OH
Cl

(V)

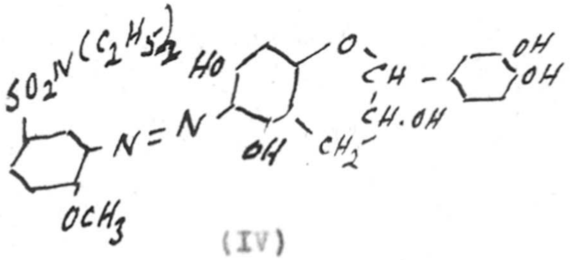


(VII)

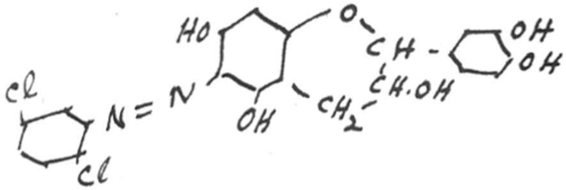
Modifications have been effected in the conditions of coupling and the mono azo derivatives (II), (IV) and (VI) have been prepared



(II)



(IV)



(VI)

This is an important observation in view of the possibility of catechin being thus converted into a hexahydroxy analogue, which should be valuable for the production of black shades.

Khaki shades from cutch: While there are several Indian and foreign varieties of cutch, which is a mordant dye, the polygenetic character of the dye is recognised as being within restricted limits. Until recently when Ramachandran and Venkataraman (Ind. P., 24,056) described processes for the production of a larger variety of shades from cutch by applying it in conjunction with diazo salts, only browns were available. It has now been found (Ind. P. 26,980) that by addition of certain mordants and adoption of modified processes, shades other then the usual browns could be obtained even without resorting to the coupling reaction with diazo salts.

The process consists in using the indigenous dyestuff, cutch, in combination with a chromium salt, such as chromium acetate or chrome alum neutralised with sodi acetate, in which the chromium is present as the positiv radicle (as distinguished from chromates and dichromates in which the chromium is part of the acid radicle), and the material, after it is padded through the cutch bath containing the chromium salt, is subjected to suitable after-treatment, such as with copper sulphate or dichrom dilute sodium silicate solution, soap or synthetic resin producing combinations, such as casein and formaldehyde.

Khaki shades similar to mineral khaki ranging from the greenish to the brownish have been produced, the concentration of metallic mordants being considerably le than that usually employed in practice for the productio of mineral khaki shades. Fabrics dyed by this process a characterised by suppleness and softness usually not met in the case of mineral khaki; the shades comparing favou bly in fastness properties with the latter.

EXPERIMENTAL

Isolation of catechin from Pegu cutch: Catechin was obtained by the method described by Perkin and Yoshitake (loc. cit.), in which the finely powdered Pegu cutch (30 g.) (obtained from Merck) was extracted with boiling ethyl acetate (300 c.c.) in a Soxhlet, the extract filtered off and the solvent evaporated. The residue was once crystallised from water, the crystals re-dissolved in boiling water and treated with lead acetate solution till a coloured precipitate ceased to appear. This was filtered and into the hot filtrate sulphuretted hydrogen was led in and the lead sulphide filtered off. The filtrate obtained in this case was almost colourless and when concentrated and cooled, very pale pinkish-brown coloured crystals (10.6 g.) melting at 200-202°C. were deposited (cf. Perkin and Everest, "The Natural Organic Colouring Matters, p. 471), m.p. for acacatechin 204-205°C.).

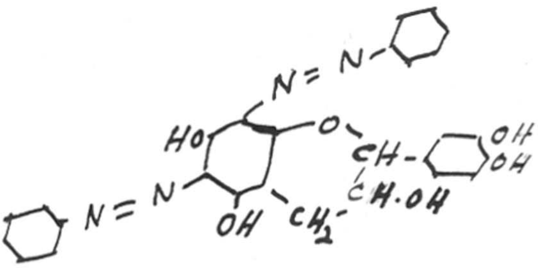
Since the above method was not found to ~~the~~ be quite expeditious, extraction at the room temperature (30°C.) with ether was tried. The powdered cutch (50 g.) was shaken up with ether (250 c.c.) in a separating funnel for one hour and left overnight. A yellow brown ethereal layer separated and was decanted off. This process of extraction was repeated thrice, using the~~s~~ same quantity of ether each time, but the time of contact was curtailed to one hour. The ether layers were collected together an ether distilled off. A light brown coloured product resulted which was recrystallised from water. The almost colourless catechin (14.2 g.) gave a melting point identic with the above.

Characterisation of the catechin from Pegu cutch:

To characterise the catechin obtained from Pegu cutch, the acetyl derivative was prepared. Catechin (2 g.) was refluxed for 3 hours with acetic anhydride (10 c.c.) and pyridine (10 drops), the reaction product poured into cold water, the precipitate obtained, crystallised from alcohol containing a few drops of acetone. The colourles needles of penta-acetyl catechin, melted at 159-60°C. (cf. Perkin and Everest, *loc. cit.*, melting point of pent acetyl acacatechin 158-60°C.). This was found to be dext rotatory, having a specific rotation of $[\alpha]_D^{31^\circ} + 7.5^\circ$

Preparation of azo dyes from catechin.

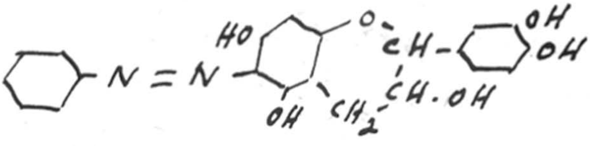
Disazobenzene catechin (I):-



(I)

Catechin (2 g.) (1 mol.) was dissolved in warm water (50 c.c.) and cooled to roomvs temperature (30°C.); to this was added aniline (1.4 g.) (2.2mols) diazotised in the usual manner. The dye (2.8 g.) was crystallised from glacial acetic acid in salmon coloure needles which melted with decomposition at 198°C. (cf. Perkin and Yoshitake, loc. cit., m.p. of azobenzene catechin 198-200°C.). (Found: N, 11.1. $C_{27}H_{22}O_6N_4$ requires N, 11.2%).

5(or 7)-Monoazobenzene catechin (II):

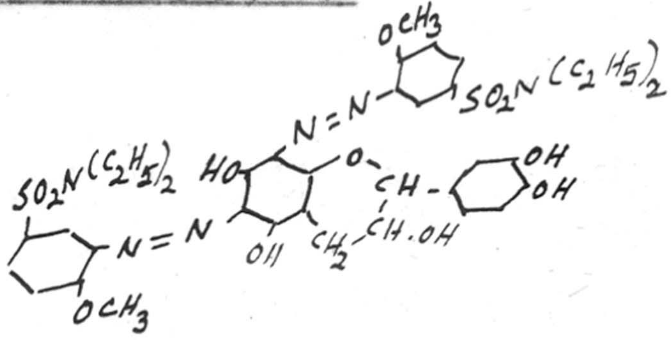


(II)

To catechin (2 g.) dissolved in water (50 c.c.) was added sodium acetate (10 g.) in water (25 c.c.). Into this was added diazotised aniline (1.4 g.) the final volume after the addition of this being kept belo 200 c.c. The dye that separateds crystallised from acetic acid as red brown tiny needles (2.2 g.) which decomposed at 203°C. (Found: N, 7.2. $C_{21}H_{18}O_6N_2$ requir N, 7.1%).

Repetition of this above reaction using sodium hydroxide 32.5% (1.c.c.) in place of sodium acetate resulted again in a monoazo derivative being obtained. Crystallisation from acetic acid gave dark brown needles decomposing at 204°C. (Found: N, 7.9. $C_{21}H_{18}O_6$ requires N, 7.1%).

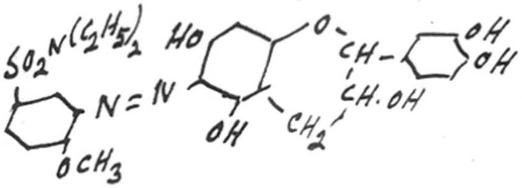
<u>Bis-5:7-(2'-methoxy)benzeneazo catechin-5':5'-N:N-diethylsulphonamide (III):</u>



(III)

3-Amino~~-4~~-4-methoxy benzene-5-sulphondiethylamide (3.9 g.) (2.2 mols) was mixed with water (40 c.c.) to which hydrochloric acid 32% (4 c.c.) was added; this was cooled to 10°C. and sodium nitrite (1.2 g.) dissolved in water (20 c.c. was added to this and the diazotisation allowed to proceed for 15 minutes at 10°C. To this was added sodium acetate (2.5 g.) dissolved in water (30 c.c.) an the volume made up to 150 c.c. with water. This diazo solution was mixed with the solution of catechin (2 g.) in water (50 c.c.). The dye that separated was treated with boiling water and crystallised from a mixture of glacial acetic acid and alcohol. The red brown needles (3.4 g.) did not melt below 250°C. (Found: S,75; N, 9.7. $C_{37}H_{44}O_{12}N_6S_2$ requires S, 7.7 and N, 10.1%).

Mono-5 (or 7) (2'-methoxy) benzeneazo catechin-5'-N:N-diethyl-sulphonamide (IV):

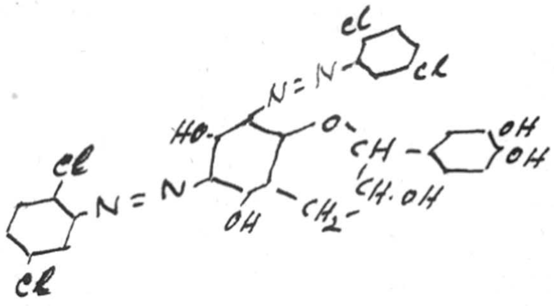


(IV)

o-amino-5-sulphondiethylamide (3.9 g.) diazotised as above, was added to catechin (2 g.) dissolved in water (50 c.c.) to which an addition of sodium acetate (10 g.) had been made. The resultant dye was treated with boiling water and crystallised from acetic acid. Ther red brown coloured needles (2.9 g.) did not melt below 250°. (Found; S, 5.4; N, 8.0. $C_{26}H_{29}O_9N_3S$ requires S, 5.7 and N, 7.5%).

Repeated as above but with sodium hydroxide 32.5% (1 c.c.) replacing sodium acetate, a dye (2.5 g.) was obtained. This gave on crystallisation with acetic aci red brown needles which did not melt below 250°C. (Found: S, 5.9. $C_{26}H_{29}O_9N_3S$ requires S, 5.7%).

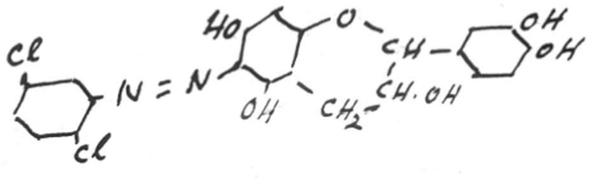
Bis-5:7(2':5'-dichloro)benzeneazo catechin (V):



(V)

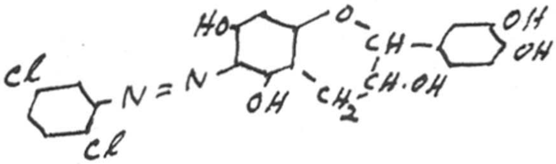
2:5-Dichloraniline (2.2 g.) (2.2 mols.) was stirred with a mixture of hydrochloric acid 32% (4.5 c.c.) and water (15 c.c.) and allowed to stand for 15 minutes. This was then cooled to 10°C. and poured in a thin stream into sodium nitrite (0.9 g.) dissolved in water (30 c.c.), allowed to stand for 10 minutes and filtered. To the filtrate was added sodium acetate (5.5 g.) dissolved in water (40 c.c.) and the volume made up to 150 c.c. with water. This was added to catechin (2 g.) in water (50 c.c.). The dye obtained was treated in the usual way with boiling water, and crystallised from acetic acid in brown needles which softened at 210°C. but did not melt below 250°C. (Found: Cl, 22.8. $C_{27}H_{18}O_{6}Cl_{4}N_{4}$ requires Cl, 22.3%).

Mono-5(or 7) (2':5'-Dichloro)benzeneazo catechin(V



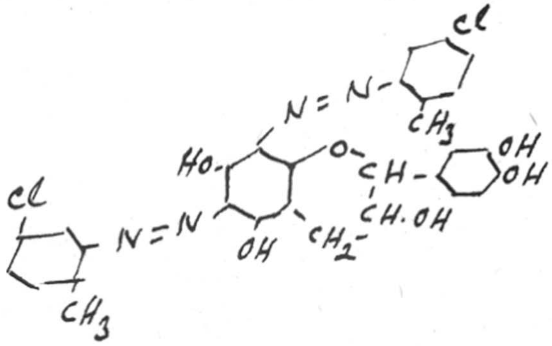
(VI)

Catechin (2 g.) was dissolved in water containing sodium acetate (10 g.) and coupled with diazotised 2:5-dichloraniline (2.2 g.) as above. The dye crystallised from acetic acid in orange coloured tiny needles. (Found: Cl, 14.9. $C_{21}H_{16}O_6N_2Cl_2$ requires Cl, 15.3%).



Reaction carried out as above but with the sodium acetate replaced with sodium hydroxide 32.5% (1 c.c.).

Bis-5:7-(2'-methyl-5'-chloro)benzeneazo catechin(V



(VII)

To 4-chloro-2-aminotoluidine (2.1 g.) was added warm water (50°C.) (25 c.c.) and hydrochloric acid 32% (2.2 c.c.) the solution filtered through a five fabric mixed with water set at 10°C. (50 c.c.). To this was added (0.9 g.) of sodium nitrite dissolved in water (15 c.c.); diazotisation was allowed to proceed for 30 minutes at 10°C. and the solution filtered. To this wa added sodium acetate (1.6 g.) dissolved in water (10 c. This diazo solution was run into catechin (2 g.) kept dissolved in water. The final volume was maintained wi 200 c.c. The dye that separated was treated with hot water as in previous cases, and crystallised from dilut acetic acid in small needles (2.8 g.) in brick red in appearance, melting at 212°C. (Found: Cl, 11.5. $C_{29}H_{24}O_6Cl_2N_4$ requires Cl, 11.9%).

Dyeings on yarn: Except where otherwise stated, the cutch used in the following experiments was a sampl termed "Cutch for Dyeing" manufactured by Indian Wood Products Ltd., Izzatnagar, United Provinces. Single 20's yarn, wetted out and hydroextracted, was treated with a solution containing 10% of cutch and 1% of coppe sulphate, calc. on volume; the material-liquor ratio wa 1:30. The yarn was worked for 1 hour at the boil and fo

30 minutes in the cooling bath. It was then washed and soaped at the boil with 0.2% soap solution for 30 minutes.

The dyed yarn was developed in a 12% solution of Fast Blue Salt BB and of Fast Black Salt K, respectively, for 10 minutes, washed and soaped. The original chestnu shade had altered to deep nigger brown and deep peat-brown respectively.*

In order to determine the minimum concentration of diazo salt required for a given dyeing, yarn impregnated with cutch and unchromed was developed with 1, 1.5, 2, 4 5 and 8% solutions of Fast Blue Salt B, the time of coupling being 10 minutes. On washing, soaping and dryi the samples as usual, it was found that the maximum development of shade had taken place in the case of the 4% solution and no further increase in depth was effecte by increasing the concentration of the diazo solution. In subsequent experimentsin which yarn dyed from a 10% solution of cutch was after-treated with a diazo salt, a

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* In naming the shades, use has been made of the British Colour Council Dictionary of Colour Standards, 1934.

strength of solution of the latter corresponding to 4% of Fast Blue Salt B was employed. When, however, yarn was dyed a 10% shade of cutch on the weight of the material, it was found that 2% solutions of the diazo salts were usually sufficient to give full development.

A series of dyeings was made with and without sodium acetate (4% on volume) to study the alterationsin shade in the case of a number of diazo salts (Table I). The samples were washed, chromed with 2% bichromate solution at the boil for 15 minutes, washed and soaped for 15 minutes with 0.2% soap solution. The effect of chroming on the shade was marked. Thus, the cutch dyeings develop with Fast Orange Salt GR changed on chroming from a red brown to a deep bluish brown; with the addition of sodium acetate to the developing bath, the effect of chroming wa to change a yellow brown to a deeper shade of bluish brown.

Table I/

Table I

Fast Salt of Base	Shade	
	Without sodium acetate	With sodium acetate
Yellow GC	Bluer-brown than Murrey	Deep shade of beech-brown
Scarlet R	Deep purple-brown	Purple brown
Scarlet GG	Deep purple-brown	Purple brown
Orange GR	Deep bluish-brown	Deeper bluish-brow
Orange GC	Purple-brown	Deep purple-brown
Red RC	Purple-brown	Purple-brown
Red B	Chocolate	Deep purple-brown
Red GL	Purple-brown	Deep purple-brown
Red TR	Much deeper than Murrey	Bluish purplish brown
Red RL	Chocolate	Purple-brown
Bordeaux GP	Chocolate	Purple-brown
Garnet GBC	Red-brown	Murrey
Violet B	Purple-brown	Deep purple-brown
Blue B	Deep purple brown	Chocolate
Blue BB	Deep purple-brown	Chocolate
Blue RR	Purple-brown	Burgundy
Variamine Blue B	Deep nigger-brown	Brown-black
Black K	Nigger-brown	Deep nigger-brown

The dyeings described in Table I represented deep shades produced from a 10% solution of cutch. In a second series of dyeings (Table II), 10% of cutch on the weight of the material was employed, the material-liquor ratio and the conditions of dyeing being unchang The concentration of the cutch bath was thus 0.33% by volume, i.e. 30 times weaker than the first bath. After dyeing, the yarn was developed in a solution of 2% diazo salt and 4% sodium acetate; one half of the yarn in the case of each diazo salt was unchromed and t other half chromed; both were submitted to the usual soaping treatment.

Although the starting bath of cutchwas 30 times weaker than in the previous experiments, the ultimate shades after development with diazo salts were very muc less than 30 times weaker. The economy of the coupling method in the production of full shades was therefore apparent.

Table II/

Table II

Fast Salt or Base	Shade	
	Unchromed	Chromed
Salts:		
Yellow GC	Brownish-yellow	Golden-brown
Scarlet R	Rust	Copper-brown
Scarlet GG	Brownish-yellow	Golden-yellow
Orange GR	Yellow-brown	Golden-brown
Orange GC	Golden yellow-brown	Deep golden-yellow-brown
Red RC	Rust	Copper-brown
Red B	Horse chestnut	Copper-brown
Red GL	Red brown	Rust
Red TR	Yellow brown	Rust (deeper)
Red RL	Deep shade of mace	Golden brown
Bordeaux GP	Terra cotta	Terra cotta
Garnet GBC	Reddish brown	Deep purple brown
Violet B	Horse chestnut	Purple brown
Blue B	Purple brown	Nigger brown
Blue BB	Purple brown	Deep purple brown
Blue RR	Deep purple	Deep clove brown
Variamine Blue B	Dark brown	Clove brown
Black K	Nigger brown	Deep clove brown

Table II contd.

Fast Salt or Base	Shade	
	Unchromed	Chromed
Bases:		
Red RBE	Reddish brown	Deep purple brown
Red ITR	Pale yellow brown	Deep yellow brown
Red TR	Oak wood	Deep yellow brown
Blue BB	Oak wood	Deep purple brown
α-Aminoanthraquinone	Yellow brown	Pale purple brown
β-Aminoanthraquinone	Slightly bluish brown	Almond shell
p:*p*'-Diaminodiphenylamine	Purple brown	Slightly more purplish than peat brown
p:*p*'-Diaminodiphenylmethane	Yellow brown	Deep rust

It will be noted in Table II that with Red TR and Blue BB both the diazotised base and the corresponding stabilised diazo salt were used. In the development of a 'Naphtol' the use of a diazotised base or the stabilised diazo salt should have no influence on the shade, if the conditions of development such as the hydrogen ion concentration are similar; the fastness properties, particularly the fastness to rubbing, might be conceivably different. But in the case of cutch, a mordant dye, the replacement of the stabilised diazo compound containing metallic salts by the freshly diazotised base may make a material difference to the shade before chroming. Thus, the shades for the salt and the base respectively were - Red TR yellow-brown, oak wood; Blue BB purple-brown, oak wood (slightly paler than in the case of Red Base TR).

Cutch dyeings on cloth after-treated with diazo salts:

Jigger dyeing: All the dyeings were made on a low quality longcloth ('pugree'), weighing 5 lb. per piece 40 yards, 56 picks and 72 ends. The liquor was made up with 10% cutch and 1% copper sulphate on the weight of the material, the material liquor ratio being 1:40. The dyeing was carried out at the boil for 1 hour and then for 30 minutes in the cooling bath. The dyed cloth was cut into the necessary number of pieces, each piece being developed with a diazo salt. Sodium acetate was added in those cases where there was an improvement in the attractiveness and depth of shade produced. Each sample was then cut in two, one half being chromed with 2% potassium bichromate at the boil for 15 minutes, washed and soaped, and the other being only soaped.

Following the Society's method (Society of Dyers and Colourists, Report on the work of its Fastness Committee, 1934), the light fastness of the dyeings was examined (Table III, column 4). The favourable effect of chroming on light fastness was clear in every case.

Table III

Fast Salt or Base	Shade		Light fastn chrom sampl
	Unchromed	Chromed	
Orange Salt GC	Yellow brown	Deeper brown	3-4
*Scarlet Salt GG	Deep yellow brown	Golden brown	2-3
Scarlet Salt GG	Pale yellow brown	Deeper dull brown	2-3
*Red Salt RC	Deep golden brown	Deeper brown	3
Red Salt RC	Pale golden brown	Deeper ~~and~~golden ~~bluer~~ brown	1-2
Red Base RBE	Golden brown	Deeper and bluer brown	4-5
Red Base ITR	Yellow brown	Purple brown	4
*Blue Salt BB	-	Deep purple brown	4
*Blue Salt RR	Pale purple brown	Deep purple brown	4
Blue Salt RR	Reddish brown	Deep purple brown	3
Variamine Blue B	Nigger brown	Deep nigger brown	3-4

The dyeings from Blue Salt RR and Red Salt RC showed that coupling under the right conditions was necessary not only for the production of the desired shade, but also for improving the fastness properties.

Padding with cutch and coupling with diazo salts:

In addition to the obvious disadvantage of the time tak by the recognised methods of dyeing cutch, such dyeings are not best suited for after-treatment with diazo salt Samples which have gone through the two stages of dyein and fixation with copper sulphate and bichromate, in which therefore the dyestuff is no longer present as catechin, do not readily couple with diazo salts; the process is slow and the duplication of results has presented certain difficulties with regard to the precise state of oxidation of the catechin. A padding method was therefore employed in later experiments.

Using a small two-bowl padding machine, low quality longcloth was first padded at 85-90°C. through a liquor containing 3% cutch and 2% sodium acetate on t volume, only one passage being given and the pressure on the pad mangle being adjusted to give a 100% squeezing effect. The cloth was then dried at 60°C. in a hot air flue; drying at a moderate temperature was necessary to avoid oxidation of the catechin as far as possible. The cutch padded piece was then padded through a 5% solution of a diazo salt and aired for 15 minutes to ensure complete coupling. Each piece was then cut in two, one-half being treated for 15 minutes at 60°C. with a solution of 0.06% bichromate and 0.03% copper sulphate; the other half was left unchromed; both were washed and soaped for 15 minutes with boiling 0.25% soap solution.

In addition to a series of commercial bases and salts and simple bases, e.g. aniline, *p*-nitraniline, α- and β-naphthylamine, the cutch-padded cloth was also developed with the diazo salts of α- and β-aminoanthraquinone, 4:4'diaminodiphenylmethane, 4:4'-diaminodiphenylamine and 1:5diaminoanthraquinone. The diazotisations were effected by treating the solutions or suspensions of the bases in glacial acetic acid with sodium nitrite and concentrated sulphuric acid (Hodgson, *J. Chem. Soc.*, 1933, 1620; Schoutissen, *J. Amer. Chem. Soc.*, 1933, *55*, 4537). α-Aminoanthraquinone gave a dark red solution in boiling glacial acetic acid, which on cooling deposited a flocculent precipitate; when this was added to sodium nitrite in sulphuric acid, a white mass separated, which did not dissolve on stirring, but immediately dissolved on dilution. The solution of the diazo salt was reddish orange in colour. β-Amino anthraquinone did not dissolve in glacial acetic acid, but, when the suspension was treated with sodium nitrite and sulphuric acid, it immediately dissolved. Dilution gave a small amount of a scum which was filter off, yielding a bright crimson red solution. The clear solution of diaminodiphenylmethane in glacial acetic acid gave a claret red diazo solution. Diaminodiphenylamine was sparingly soluble in glacial acetic acid, but with sodium nitrite and sulphuric acid, a yellow green solution was obtained. The cloth prepared with Naphtol AS on development with this diazo solution came out yellow first, changed to pale brown, then to purple and finally to a magnificent blue. 1:5-Diaminoanthraquinon was insoluble in glacial acetic acid, but readily dissolved after treatment with sodium nitrite and sulphuric acid, followed by dilution. The respective shades obtained with these five diazo solutions on Naphtol AS grounds were geranium, pink, cherry, murrey, deep mineral blue and cardinal. According to Maki

(J. Soc. Chem. Ind., Japan, 1931, 34, 427B; Jap. Pat. 89,162; 89,163), fast red shades were obtained by coupling diazotised α- and β-aminoanthraquinones with Naphtol AS, AS-BS and AS-BO; β-aminoanthraquinone yielded much brighter shades.

The shades obtained on the cutch-padded ground are recorded in Table IV.

Comparison of jigger-dyed and padded samples disclosed considerable differences in the dyeings obtained by the two methods, the advantage being always on the side of the padding method with regard to the desirability and brightness of the shades. With regard to fastness to light and to washing, the padded samples compared favourably with the jigger-dyed samples.

The influence of buffers on the shade is shown in Table V. Cloth was padded with a 1% solution of cutch at 85°C. and dried in the hot flue at 60°C. Portions of the cloth were then developed respectively with diazotised α-naphthylamine and Fast Blue Base BB, additions of various buffers being made. α-Naphthylami (30 g.) was diazotised with sodium nitrite (18 g.) and 32% hydrochloric acid (72 c.c.). Fast Blue Base BB (30 g.) was diazotised with sodium nitrite (7 g.) and 32% hydrochloric acid (27 c.c.). Each diazo solution

Table IV

Salt or Base	Shade	
	Unchromed	Chromed
Yellow GC	Tangerine	Golden brown, but slightly darker
Orange GC	Tangerine	Golden brown
Orange GR	Yellow brown	Golden brown,sligh redder but deeper
Scarlet GG	Golden yellow	Golden brown
Scarlet R	Rust	Golden brown
Scarlet TR	Yellow brown	Golden brown
Red TR	Marigold, but slightly browner	Reddish golden bro
Red KB	Golden yellow	Golden brown
Red B	Terra cotta	Horse chestnut
Red ITR	Slightly browner than tangerine	Mace, but deeper
Red RC	Bright reddish brown	Deep golden brown
Red RBE	Bright orange brown	Copper brown
Red GL	Rust	Dark golden brown
Red RL	Yellow brown	Dark golden brown
Garnet GBC	Coral	Terra cotta
Bordeaux GP	Horse chestnut	Purple brown
Violet B	Redder than horse chestnut and deeper	Murrey
Blue B	Chocolate	Chocolate
Blue BB	Purple brown	Very deep purple b

Table IV contd.

Salt or Base	Shade	
	Unchromed	Chromed
Blue RR	Burgundy	Burgundy, but paler
Variamine Blue B	Black brown	Very deep purple br
Corinth V	Purple brown	Purple brown
Black K	Nigger brown	Bluish chocolate
Aniline	Golden brown	Olive brown
p-Nitraniline	Purple brown	Chestnut
α-Naphthylamine	Pale golden brown	Dull olive brown
β- "	Bluer brown	Dull brown
α-Aminoanthraquinone	Pale golden brown	Dull brown
β- "	Deeper shade of rust	Dull brown, slight more yellowish th with α-aminoanthr quinone
4:4'-Diaminodiphenylmethane	Deeper shade of rust	Olive brown
4:4'-Diaminodiphenylamine	Deep pink	Beech brown
1:5-Diaminoanthraquinone	Rust	Olive brown

was bulked to 2,000 c.c., 200 c.c. of the solution neutralised with sodium bicarbonate and treated with 1 g. of one of the substances listed in Table V. The cutch-padded cloth was developed with the solutions and after-treated as usual.

Table V

Buffer	Shade α-Naphthylamine Before chroming	 After chroming
Blank	Deep rust	Deep golden brown
Sodium acetate	Deep rust	Deep golden brown
Disodium hydrogen phosphate	Deep terra cotta	Deep bluish brown
Sodium meta-phosphate	Yellow brown	Pâle bluish brown
Sodium hexa-metaphosphate	Pale terra cotta	Bluish brown
Sodium pyro-phosphate	Reddish terra cotta	Deep bluish brown
Sodium di-hydrogen phosphate	Weak rust	Deep golden brown
Trisodium phosphate	Deep terra cotta	Deep bluish brown

Table V contd.

Buffer	Shade Blue Base BB Before chroming	 After chroming
Blank	Purple brown	Chocolate
Sodium acetate	Murrey	Deep chocolate
Disodium hydrogen phosphate	Pale murrey	Deep purple brown
Sodium metaphosphate	Pale murrey	Purple brown
Sodium hexametaphosphate	Pale murrey	Pale murrey
Sodium pyrophosphate	Pale murrey	Deep purple brown
Sodium dihydrogen phosphate	Pale murrey	Purple brown
Trisodium phosphate	Pale murrey	Deep purple brown

Cutch at 85°C. and drying in the hot flue at 60°C. the cloth was re-padded through a solution of 5% diazo-salt and 2% chromium acetate, aired for a few minutes, and steamed for 1 hour without pressure in the steaming cottage. This treatment deepened and brightened the shades, but tendering occurred in five cases, viz. Fast Orange Salt GR, Yellow GC, Red B, Red GL and Scarlet R, but only to a slight extent in the last instance. For this reason the shades obtained after soaping are not recorded in Table VI for these five salts.

Table VI

Salt	Shade before steaming	Shade after steaming	Shade after soaping
Yellow GC	Tangerine	Deep golden brown	-
Orange GC	Deep tangerine	Light golden brown	Light golden brown,slight yellow
Orange GR	Lighter and yellower than rust	Deep mace	-
Scarlet GG	Deep tangerine	Deep golden brown	Deep golden brown
Scarlet R	Rust	Redder than mace and deeper	-
Red RC	Deep rust	Deeper rust than the unsteamed sample	Rust
Red TR	Yellowish rust	Light rust	Light rust
Red RL	Deep tangerine	Deep mace	Deep mace
Red GL	Deep rust	Deep rust	-
Red B	Light horse chestnut	Deep copper brown	Light copper brown
Garnet GBC	Light terra cotta	Light copper brown	Light copper brown
Corinth V	Light purple brown	Deeper purple brown	Deep purple brown
Blue B	Murrey	Pruple brown	-
Blue BB	Purple brown	Deeper purple brown	Deep purple brown
Blue RR	Light chocolate	Deep chocolate	Chocolate
Variamine Blue B	Chocolate	Pale burgundy	Burgundy
Black K	Light nigger brown	Deep nigger brown	Deeper and bluer than

The tendering could not be related to the acidity of the diazo salts concerned in comparison with the innocuous salts (Table VII).

Table VII

Fast Salt	pH of 5% solution	
	Fresh	After 20 hours
Orange GC	3.01	2.34
Orange GR	3.82	3.34
Red TR	3.92	3.30
Red B	3.39	2.97
Red GL	3.60	2.54
Yellow GC	3.79	3.34
Scarlet R	3.76	2.99
Bordeaux GP	3.70	2.99
Blue B	3.47	2.89
Variamine Blue B	3.60	3.04

The tendering, however, was completely eliminated by the addition of suitable quantities of sodium acetate to the cutch padding liquor or the developing bath. Thus, by padding with 1% cutch and 2% sodium acetate, developing with 2% diazo salt and 2% chromium acetate, and steaming, the shades recorded in Table VIII were obtained, the fabric undergoing no damage.

In order to compare different methods of after-treatment of the coupled dyestuff, cloth padded with 5% cutch and developed with 5% diazo salt, 2% sodium acetate and 2% chromium acetate, was (I) dried sharply over drying cylinders, (II) dried and aged in the Rapid Ager for 4 minutes at 100°C., or (III) dried and steame in the steaming cottage for 1 hour without pressure. A were then soaped as usual. In Table IX (I), (II), and (III) refer to these three processes.

Table VIII

Salt or Base	Shade before steaming	Shade after steaming	Shade after soaping
Yellow GC	Golden brown	Golden brown	Deep golden brown
Orange GR	Dark mace	Bluish golden brown	Bluish rust
Red B	Deep terra cotta	Copper brown	Copper brow
Scarlet R	Rust	Yellow rust	Deep rust

Table IX/

Table IX

Fast Salt	Shade			Light fastness			Rubbing fastness		
	I	II	III	I	II	III	I	II	III
Orange GC	Yellower than copper brown	Deep than (I)	Identical with (II)	2-3	3-4	3-4	3-4	3-4	4
Orange GR	Murrey	Murrey	Murrey, lighter than (I) & (II)	3-4	3-4	4-5	2-3	2-3	4
Red TR	Chocolate	Purple brown	Purple brown, weaker than (II)	2-3	3	3-4	2-3	3	3-4
Red B	Oakwood	Deep golden brown	Deep golden brown	3-4	3-4	3-4	3-4	3-4	4
Blue B	Copper brown	Deep golden brown	Deep golden brown, redder than (II)	3-4	3-4	4	3-4	3	3-4
Variamine	Nigger brown	Nigger brown, deeper than (I) & (II)	Nigger brown	5	5	5	3-4	2-3	3

The omission of the ageingt treatment gave slightl deeper, but duller shades; there were only minute differences noticeable between the samples aged in the Rapid Ager and in the cottage, the latter being somewh brighter.

In general, the shades obtained by the chromium acetate method were characterised by their brightness, but the light fastness was only moderate and the dyein were inferior in this respect to those obtained by the cutch-sodium acetate padding method involving after-treatment of the coupled dyes with copper sulphate and bichromate (Table IV).

<u>Printing experiments:</u> Although no mention is made in the literature of the use of diazo salts in conjunction with cutch in calico printing, results of practical interest were obtainable by this means, as indicated in the following examples. (1) The low quality longcloth used in the dyeing and padding experiments was padded with 0.25% cutch solution containing 2% sodium acetate at $85-90^{\circ}C$. and dried at $50-60^{\circ}C$. in the hot flue. The material was printed with a 5% solution of Fast Orange Salt GC in a thickeni

of 15% British gum, dried, and the ground developed with a 1% solution of Fast Blue Salt BB to give a yellow-brown print on a purple background. (2) Using Fast Black Salt K for printing and Fast Scarlet Salt GG for the ground shade, a pleasing effect of a yellow background and a dark brown overprint was obtained. (3) In a similar experiment Variamine Blue Salt B and Fast Violet Salt B were respectively employed for the print and the ground shade; the result was a dark brown print on a rust background. (4) Cloth padded through 0.5% cutch solution containing 2% sodium acetate and dried was spray printed in a three colour design with three diazo salts, viz. 5% Scarlet GG, 3% Red B and 5% Blue BB in a starch-tragacanth thickening. The ground was partially cleared by treating the printed pieces in the cold for 10 minutes with a 2% solution of acetic acid (30%), washing and soaping. Deep golden brown, yellow and dark brown prints, fast to rubbing, on a very pale red-brown ground were the ultimate result. Similar harmonious colour effects were producible by printing with diazo salts and chromium acetate on cutch-padded cloth, followed by two passages (10 minutes) in the Rapid Ager; the brightness of the prints was considerably improved by this method. Pleasing effects were also obtained by printing on a cutch bottom with one diazo salt and developing the ground with a second. Whilst the range of colourings were naturally limited, the fastness to rubbing was excellent and the limitations with regard to the colour scale were a favourable factor in so far as a quiet and harmonious colour scheme was automatically accomplished This was at once apparent from an inspection of samples in which three diazo salts, viz. Scarlet GG, Red B and Blue BB, were printed on cloth impregnated respectively with cutch and Naphtol AS. The process was specially suitable for spray printing.

Khaki shades from cutch: Dye trials were carried out on drill weighing 18 lbs. for 40 yards. The material was scoured by boiling in a high pressure kier using caustic soda (4%) on the weight of the material and Igepon T (0.25%) at 30 lb. pressure for 8 hours, washed thoroughly and dried. Padding through the impregnating bath was carried out in two-bowl padding machine of the standard Mather and Platt type, the pressure between the bowls being adjusted to give 100% squeeze.

For purposes of experiment, three varieties of cutch have been used, the essential difference between them lying in their catechin content, to test if all give shades of khaki. While khaki shades are obtainable from all of them, greener shades would seem obtainable only from varieties having high catechin content. Thus among the three varieties chosen, Kheersal (80-85% catechin) gave greener shades than either "pale cutch" or "cutch for dyeing" having catechin contents 50-52 and 45% respectively.

1. "Pale cutch" (10 g.) was dissolved in boiling water to which chromium acetate (50 g.) was added. The temperature of the bath was raised to 70°C. and the fabric padded through so as to get two dips and two squeezes, dried in a hot flue steamed in the Rapid Ager for 12 minutes and chromed at the boil for 30 minutes using sodium dichromate (0.3%) and copper sulphate (0.2%) and washed. The fabric was subsequently treated at boil for 15 minutes in a solution of sodium silicate (2%) washed and dried. This gave a greyish green khaki.

2. In a second set of experiments the scoured

material was padded through a padding liquor consistin of pale cutch (15 g.), hot water (300 c.c.), chromium acetate (75 g.) and ferrous sulphate (4 g.), steamed f 30 minutes in the steaming cottage, treated for 1 minute in a boiling solution of soda ash (2%) and washe This was then chromed for 30 minutes at the boil in a solution made up with copper sulphate (0.1%) and potassium dichromate (0.2%) and otherwise processed as in (1). A khaki very much akin in shade to the popular mineral khakis on the market was obtained.

3. Repeating operation (1) using Kheersal in place of pale cutch resulted in a khaki shade much greener than obtained in (1).

4. "Cutch for dyeing" (10 g.) dissolved in water (300 c.c.) was mixed with chromium acetate (60 g.) dissolved in water (500 c.c.) and iron acetate (30 g.) and the final volume made up to 1 litre with water. Scoured drill was padded through the liquor in a padding mangle set for a 75% squeeze and given four dips and four nips, dried over steam heated drying cylinders. The material was steamed in the Rapid Ager for 4-5 minutes and worked in a jigger at the

boil for 30 minutes in a solution of sodium dichromate (0.5%) and Igepon T (0.25%), and washed in cold water. This was ~~filtered~~ followad up by a treatment on the jigger in sodium hypochlorite set at 2 g./litre for 15 minutes. The material was then soaped for 30 minutes at boil using a solution containing caustic soda flakes (0.5%) soap (1%) and sodium silicate (2%), washed and scoured at 50°C. for 10 minutes in the jigger using glacial acetic acid (0.25%), washed in water and dried. A khaki slightly on the brownish side resulted. The dye samples were tested for their fastness to washing, chlorine, acid, perspiration and light. In assaying the fastness properties, except towards light, the method specified by the German Echtheitskommission hav been adopted. The light fastness tests were carried o by the method described by Bhat and Ramachandran (*J. I Chem. Soc., Indl. Ed.*, 1942, 5, 11). Chromium and iro were estimated by the usual procedures. For purposes of comparison two shades of mineral khaki dyed by firms reputed to specialise in this trade and approximate in shade to the cutch samples were taken.

Estimation of chromium and iron: The samples (after a preliminary boil in water for a period of 30 minutes in thecase of the mineral khaki samples to remo any washable impurities) were cut into pieces less than 1/4" square and dried at 110°C. to constant weight.

About 3-4 g. of the dry samples were transferred to a previously dried and weighed nickel crucible and ashed gently at first for 20 minutes using a Bunsen flame, followed by heating in an electric muffle furnac at 750-800°C. for 1 1/2 hours. After cooling in a desiccator, the ash in the crucible was carefully mixed with 8-10 times its weight of sodium peroxide and furth fused for a period of 15 minutes and cooled. The crucible with its lid was placed in a tall 600 c.c. bea and covered with a watch glass. Distilled water (150 c.c.) was then slowly introduced along the sidesof the beaker. After the reaction in the beaker had subsided, the contents were boiled for 20 minutes, the crucible and lid removed and rinsed with cold water, the rinsing being added to the beaker. A fresh quantity (0.5 g.) of sodium peroxide was taken in the crucible fused, and the washing repeated. The liquor in thebeaker was ~~in~~ b for 30 minutes, and filtered. The filter paper was washed with hot water and the volume made up to 500 c.c.

The precipitate on the filterpaper was dissolved in hot dilute sulphuric acid (25%), the ferric sulphate reduced with stannous chloride and the excess of the latter being destroyed by the addition of mercuric chloride. The beaker with its contents was allowed to stand for 10 minutes and titrated against standard ceric sulphate, using o-phenanthrolein ferrous complex as indicator.

For the estimation of chromium, an aliquot part of the liquor was pipetted out into a conical flask and an excess of ferrous ammonium sulphate of known strength w added. The contents of the flask were made acidic with sulphuric acid and the excess of ferrous ammonium sulphate titrated against ceric sulphate.

Fastness properties:

Fastness to washing: was carried out as follows: Two parts by weight of the dyed material was stitched on to bleached calico of about the same weight and boiled for 30 minutes, the solution containing 5 and 3 g./ litre of Marseilles soap and soda ash respectivel using a material liquor ratio of 1:50. The liquor was allowed to cool down within 30 minutes to 40°C., the sample dipped ten times in the liquor and after each dip well squeezed. It was thoroughly washed in cold water and dried.

Fastness to acid: Dyed material 2" x 2" was wetted out in hot water, mangled to give even squeezin and dipped in 10% solution of sulphuric acid (96%) for 10 minutes at 30°C., rinsed and dried.

Fastness to perspiration: The dyed material 4" x 4' was sandwitched between two layers of white calico and rolled. It was then treated for 30 minutes at 45°C in a solution containing 5 g. common salt and 6 c.c. of ammonia (24%) per litre, the sample being squeezed at a interval of 10 minutesby hand. This process of squeezi was then repeated with the sample in 7.5 c.c. glacial acetic acid per litre, the total time of impregnation being again 30 minutes. The sample was then squeezed finally and dried without rinsing at room temperature (30°C.).

Fastness to chlorine: Two types of tests were carried out in this case. In the first case the samples were wetted out squeezed and immersed for 1 hou at 30°C. in freshly prepared sodium hypochlorite to set to give 1 g. available chlorine per litre to which 0.2 g. of sodium bicarbonate had beed added. At the end of one hour the test sample removed rinsed in water soured in dilute acetic acid, remrinsed and drie In the second case the sample was similarly treated, b in a perchloron solution containing 3 g./litre available chlorine. In all the above tests, the sampl were compared against respective standards, and assigned grades. The results are recorded in Table IX. A perusal of Table IX would indicate that cutch khaki dyed by process (4) stands favourable comparison in fastness with the mineral khaki samples A and B; the lower grade obtained in the case of light (5-6) agains sample B (7-8) may partly be explained by the difference in the nature of the fabrics (the mineral khaki dyed material in this case being heavier) and the greater depth of shade.

Table X

Table X

Sample No.	Per cent chromium and iron		Fastness grades				
	Cr_2O_3	Fe_2O_3	Washing	Chlorine	Acid	Perspiration	Light
Cutch khaki 2	2.36	0.09	3-4-	2-3	1.2	3	4-5
" 4	2.07	0.54	4-5	3	2	4-5	5-6
Mineral khaki A	5.58	0.78	4-5	3	1-2	4-5	5-6
" " B	5.99	0.98	5	4-5	3	5	7-8

A perusal of Table I would indicate that cutch khaki dyed by process (4) stands favourable comparison in fastness with the mineral khaki samples A and B; the lower grade obtained in the case of light (5-6) against sample B (7-8) may partly be explained by the difference in the nature of the fabrics (the mineral khaki dyed material in this case being heavier and the greater depth of shade.

Part IV

Fastness properties of azoic dyes

INTRODUCTION

Azoic colouring matters are generally of good to medium fastness to light, while in a majority of cases the common weakness is their poor fastness to rubbing. Presumably this defect is inherent to the process itself, as the dyeing is the result of a dual process impregnation in the Naphtol bath, the development of the pigment being effected by a passage through the diazotised amine. With any other class of colouring matters perhaps, this defect would have acted as a deterent for its large scale use. But the azoic colou on account of their wide variety of shades and excelle fastness in other directions, combined with brightness and eash of application have become indispensable to t textile industry, whose consumption of this class of colouring matters is about one fifth of the total import of synthetic dyes.

Most of the dyeing of azoic colours in this count is on yarn to be subsequently woven with unbleached yarn, to a small extent for shirting materials, and mainly to be included in the coloured headings and borders of dhoties and sarees. Fastness to light is obviously essential in a tropical country and, since t dyed yarn is woven with white and processed in the pie fastness to rubbing and to an open boil with soap and soda ash are also necessary.

In an attempt to study the factors that influence the fastness to rubbing, Williams (*J. Soc. Dyers. Col.* 1934, **50**, 204) and Blackshaw (*ibid*., 1936, **52**, 135) laid emphasis on factors such as pre-treatment of material, restricting the choice of Naphtols to the highly substantive ones, use of wetting out agents and protective colloids in the impregnating and developing baths, efficient hydroextraction after impregnation to remove the superficially held Naphtol from the materia prior to development, and an efficient rinsing ~~of~~ and soap treatment of the developed material. Henkel (*Melliand Textilber*., 1927, **8**, 871; 955; 1928, **9**, 66, 149, 501) studied the effect of pre-treatment on affinity;accordi to him the boiled Egyptian cotton absorbed 0.232 mol. Naphtol AS, boiled out cotton 0.198 mol., bleached cotton 0.218 mol. and mercerised cotton 0.335 mol. Gerstner (*Rev. Gen. Tein. Imp. Blanch. App.*, 1932, **10**, 139; 1933, 11, 821; Seide u. Kunstseide, 1933, 38, 463) demonstrated the advantages of adding Acorit (the sodium salt of a sulphonated aliphatic alcohol) over Turkey Red oil as a protective colloid. The wetting action of the added agent depended on the alkalinity of the solution. Different substances of similar surface activity and potentiometric relations showed differences as dispersing agents for "Naphtols", Acorit being especially effective. The advantages of using an effective wetting agent and protective colloid in the Naphtol bath and in the diazo bath are undoubted, but with regard to the actual degree of improvement in relation to the increased expense there are differences of opinion.

According to Scheele (Leipziger Monatsch. Textilin 1929, 44, 79, 126) rubbing fastness runs parallel to th substantivity of the Naphtol. Although this is true in some measure, it lacks experimental verification not only with regard to the absence of any quantitative relationship between substantivity and fastness to rubbing, but as is more important from the practical point of view, also in that an unsubstantive Naphtol may lead ultimately to dyeings of excellent fastness tc rubbing. By using a Naphtol of high substantivity and ough hydroextraction it is possible to minimise the me nically adhering pigment that is responsible for loose to rubbing, but it must be remembered that the formati of the surface pigment cannot be eliminated. Further in the case of the so called substantive Naphtols, the nature and degree of the attachment of the latter, and therefore, of the precipitated pigment, to cellulose a not understood. It can be stated, however, that the quantity of mechanically adhering pigment will be grea for the less substantive Naphtols; in consequence ther will be more bleeding in the soaping bath and to that extent, less substantive Naphtols are less economical in use. The vital factor, so far as the fastness to rubbing of the final dyeing is concerned, is the after-treatment. If in the earlier stages of processing optimum conditions are observed, dyeings of good fastness to rubbing could be obtained even from an unsubstantive Naphtol by suitably after-treating it.

Considerable differences in the actual extent of the soaping after-treatment required by individual azoi dyeings were observed by Lochner (*Melliand Textilber.*, 1926, *7*, 243). Fastness to light was always improved by soaping after-treatment, but a dyeing of Naphtol AS and Fast Red Salt RL required treatment for 30 minutes t develop maximum fastness, whereas a dyeing of Naphtol AS-RL and Fast Red RL was just as much improved by good rinsing in cold water as by prolonged soaping. Accordin to *B.P.* 514,069, the fastness to rubbing of azoic dyeings is improved by adding to the soaping bath a water-soluble salt of $N(CH_2.COOH)_3$ or $(HOOC.CH_2)-N-CH_2.CH_2-N(CH_2.COOH)_2$. A reagent yielding oxygen may also be added. The process is specially suitable for laps, cross-wound bobbins and warp beams.

Adam (*J. Soc. Dyers Col.*, 1936, *52*, 6), however, considered that the defective fastness to rubbing of azoic dyeings has neither been, nor is likely to be solved, and that the view that by giving the correct treatment this defect can be overcome is scarcely correct. Thus, inspite of many trials and considerable expenditure, he had not yet seen a successful bulk process worked out for a dark blue on yarn and pieces; the results were ~~s~~usually very uneven and loose to rubbing.

Blackshaw (*J. Soc. Dyers Col.*, 1935, *51*, 309) has studied the fastness properties of numerous azoic dyeing in relation to soaping after-treatment, comparing the fastness of the dyeings (1) unsoaped, (2) soaped with 3 g. neutral soap flakes with 2 g. soda ash per litre at 80°C., (3) soaped as under (2), but at the boil, with regard to light, chlorine, open kier-boiling with soda ash, and bleaching and rubbing. He considered th excessive soaping may increase looseness to rubbing, as the alkali in the soap bath may cause undue aggregation of colouring matter and accelerate migration to the outside of the fibre.

Willshire (J. Soc. Dyers Col., 1940, 56, 245) considered that while the depth of shade and the material taken for processing vitally affected the fastness to rubbing by adopting suitable methods for different combinations, by selecting the most suitable combination/and addition of suitable auxiliaries in the impregnatin and developing baths, dyeings could be produced havin satisfactory fastness properties provided, the dyeings so obtained, are after-treated with suitable concentrations of soap and Lissapol LS (a patented auxiliary product of the Imperial Chemical Industries). Additio of soda ash to the soaping bath was not advisable as i caused rubbing by excessive migration of the dye particles from the centre of the cotton fibres to the outside, where they were more easily removed by frictio

Korb (*Leipziger Monatsch. Textilind.*, 1935, 50, 171) found that the stability of Naphtol AS baths was limited even with water of slight hardness and that exclusive use of distilled water was desirable. Additions of Turkey Red oil not only did not prevent precipitation, but greatly lowered the resistance of the dyed shades to rubbing, whereas the use of fatty alcoho sulphonate rendered the stability of a bath of even 25 hard water practically unlimited. When dyeings were made immediately and suitably after-treated, all gave equally good fastness to rubbing.

Since the recognition of the vital importance of the after-treatment of azoic dyeings to light and rubbing, there has been a fair agreement as to the composition of the after-treatment bath. A concentrat soap solution (5-10 g. per litre) or a similar solutio of soap and soda ash, is commonly employed. In addition manufacturers have, of course, recommended the use of wetting and emulsifying agents. Roiger (*Z. ges Textilind.*, 1925, 28, 654) observed that addition of tannic acid to the soaping bath improved the fastness rubbing, but darkened the shade.

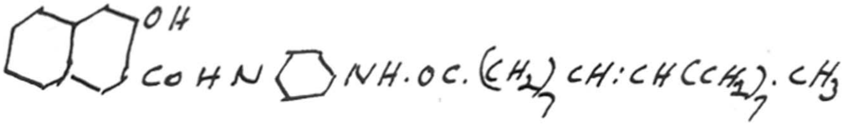
Experiments have been in progress in this laboratory on the type of auxiliary agent with reference to chemical constitution and properties, such as wetting, emulsification and protective colloidal action suitable for a given azoic combination to produce the maximum fastness to rubbing. The after-treatment is usually regarded as a process of removal by emulsification of t superficially precipitated azoic pigment formed from that part of the Naphtol not substantively adsorbed and not removed by hydroextraction; a process of solubilisation must now be assumed to be at least partially responsible for the action. Since organic compounds tend to dissolve in solvents having structural features similar to their own, the after-treatment of azoic dyeings with synthetic detergents, possessing some structural features in common with Naphtols, in additio to those which would be necessary for their behaviour as emulsifiers and detergents, has been suggested by Venkataraman (*Curr. Sc.*, 1939, *8*, 286).

One aspect in the processing of azoic colours is the poor stability of Naphtols towards hard water. Under the conditions prevailing in many of the Indian mills, this problem has often caused serious hindrance processing with consequent loss of production. The difficulties already prevalent in getting dyeings fast to rubbing in the case of Naphtols are accentuated due to the presence of calcium soaps formed by reaction between the Turkey Red oil in the Naphtol baths and the calcium and magnesium salts from the water. Another contributory factor in the same direction is the tendency of caustic soda in the Naphtol bath to lead to formation of scum where hard waters are involved. It seemed desirable therefore to replace caustic soda, partly at any rate, with products alkaline in nature, but not characterised by sensitivity towards hard water, alone, or along with other additions such as a fatty alcohol sulphonates. It was anticipated that dyeings obtained from such baths, if suitably after-treated, would lead to dyeings with greater resistance to rubbing. In view of the above considerations, dyeings have been carried out with Naphtol AS-BS and Fast Scarlet Salt GG using hard water, hardness ranging from 0-30°, using auxiliaries such as a fatty alcohol, sulphonate and trisodium phosphate. The latter has been used in view of its known ability to overcome the sensitiveness of Turkey Red oil towards calcium compounds (cf. *I.G.*

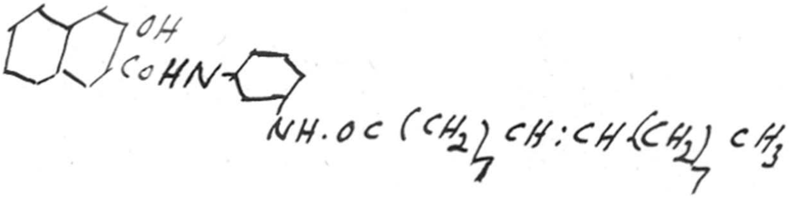
Farbenindustrie B.P. 444,071). The results are indicated in Tables I and II of the experimental part. Apart from factors such as resistance to hard water, trisodium phosphate led to shades of increased depth apparently due to the diminution in the degree of dispersion of the colloidal Naphtol.

In view of the beneficial effects of after-treatment as fastness to rubbing, and the accepted concept of its function being one of removal of the surface pigment by emulsification and solubilisation, Naphtol dyeings have now been after-treated with a series of auxiliaries known for their detergent and emulsifying action, such as the sodium salts of lauric, myristic, palmitic, stearic, linoleic, anacardic and tetrahydroanacardic acids, and also with patented auxiliaries such as Igepal C (highly polymerised compound of unknown constitution), Igepon T (sodium salt of N-methyltaurine), Nekal BX (sodium di-isopropyl naphthalene sulphonate), Gardinol WA (sodium lauryl sulphate and Aerosol OT (dioctyl ester of sodium sulphosuccinate) and the rubbing fastness of the dyeings estimated. ~~The~~For purposes of experiment, dyeing produced on yarn using Naphtol AS and Fast Blue Salt BB has been chosen in view of the well known difficulty of obtaining dyeings of reasonable fastness to rubbing in this case; the assumption being that starting with a dyeing of inferior fastness to rubbing and suitably after-treating it, the result should be a marked ascendency in the fastness scale. The results are indicated in Table III.

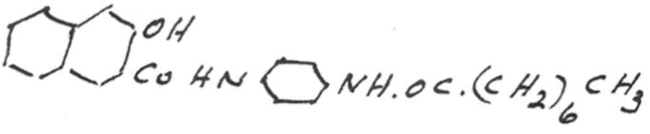
With the same object in view and with the aim of studying the effect in more specific instances where the naphthols and the auxiliary used will bear amore closer structural resemblance, dyeings from the following naphthols (I), (II) and (III)



(I)



(II)



(III)

obtained by condensing mono-N-oleyl-<u>p</u>-phenylenediamine; mono-N-oleyl-<u>m</u>-phenylenediamine and mono-N-caprylyl-<u>p</u>-phenylenediamine respectively with β-hydroxynaphthoyl chloride, have been after-treated with a mixture of sodium oleate and soap (in the case of I and II) and sodium salt of caprylic acid and soap in the case of III. Results are recorded in Table IV. In all the three cases the results indicated an improvement in the fastness to rubbing from dyeings treated with soap alone; although the increase recorded could not be construed as striking in view of the initial high degree of fastness to rubbing exhibited by these combinations on account of the existence of the aliphatic chain. In one case, however, viz. N-2-hydroxy-3-naphthoyl-N'-oleyl-<u>m</u>-phenylenediamine, the improvement recorded was quite appreciable.

EXPERIMENTAL

The yarn employed for dye trials was single 20's yarn boiled in water for 2 hours and hydroextracted. The yarn (20 g.) was impregnated in the Naphtol bath set at 15g per litre, and containing formalin 40% (1%) for 30 minutes, hydroextracted and developed in a solution of Fast Scarlet Salt GG (3%) and Diazopon A (protective colloid) (1%), washed, soured with hydrochloric acid (28%)(0.5%) for 10 minutes, washed, soaped with soap (0.25%) and trisodium phosphate (0.25%) at the boil for 30 minutes and washed. Initially the baths containing trisodium phosphate and reduced amounts of caustic soda were deeper in colour, but less transparent than the baths containing Product Y, but on standing the precipitation was more in the latter case. Series III, containing the normal amount of caustic soda and trisodium phosphate, were clearest of all. The dyeings in series I bled more in the soaping bath than those in series II, while the dyeings in series III, bled less than either I or II.

Five samples of hard water ($5-30^{\circ}$) were prepared and three sets of dyeings made: (1) the caustic soda in Naphtol bath was partially replaced by trisodium phosphate; (2) increasing amounts of a proprietary hard water resisting wetting agent (Product Y, sodium salt of N-methyltaurine) were added to the Naphtol bath; (3) using 20° hard water and the normal amount of caustic soda, additions of 0.5, 1, 2% trisodium phosphate on volume were made. In I and II the naphtholations and the observations recorded in Table II were made 18 hours after the baths were made up; and in III immediately after.

The following baths, each 400 c.c. and containing 6 g. of Naphtol AS-BS were prepared.

Table I

Series	Experiment	Hardness of water degrees	Sodium hydroxide 30% soln. in c.c.	Trisodium phosphate in g.	Product Y
I	1	0	9	0	
	2	5	6.75	2.25	
	3	10	"	2.36	
	4	15	"	2.60	
	5	20	"	2.99	
	6	30	"	3.89	

Table I contd.

Series	Experiment	Hardness of water	Sodium hydroxide 30% soln. c.c.	Trisodium phosphate in g.	Product Y
II	7	0	9		0.08
	8	5	9		0.20
	9	10	9		0.21
	10	15	9		0.25
	11	20	9		0.26
	12	30	9		0.32
III	13	20	9	2	
	14	20	9	4	
	15	20	9	8	

The appearance of the baths and the rubbing fastness of the dyeings are recorded~~d~~ in Table II.

Table II

Series	Experiment	Appearance of the baths	Rubbing fastness
I	1	Very slight precipitation; mixes upon stirring; slightly less clear than (7)	4
	2	More precipitation than in 1; same cloudiness as in (8)	3
	3	Slightly clearer and darker than (9)	3
	4	Definitely clearer and darker than ~~0~~(10)	3

Table contd.

Series	Experiment	Appearance of the baths	Rubbing fastness
	5	Much clearer and definitely less precipitation than in (11). Precipitate very finely divided	3
	6	Much clearer than (12). Precipitate finely dispersed	2
II	7	Very slight precipitation which mixes well on stirring	3
	8	Same as in (2)	2
	9	Less dark and slightly more cloudy than (3)	2
	10	Fairly clear, but less so than (4). Paler in colour	2
	11	Cloudy, precipitated badly	2
	12	Very cloudy; heavy precipitation	2-3
III	13	Clear solution	5
	14	"	5
	15	"	5

The above figures would show that even where hard water is involved, by adding suitable auxiliaries to the initial bath and suitably after-treating the material, dyeings of excellent fastness to rubbing could be obtained. Choice of a suitable auxiliary would also appear to be an important factor, judging from the inferior rubbing fastness grade of sample (11) as against samples (13, 14 or 15).

Detergent action ~~on~~ and rubbing fastness: For purposes of experiment, Naphtol AS - Fast Blue Salt BB combination was used in view of the known tendency of azoic blues to give dyeings of inferior fastness to rubbing (cf. Adam, loc. cit.). Bleached single 20's yarn was used, dyeing being carried out by impregnating for 15 minutes in Naphtol AS (2%) at room temperature (30°C.) in a material liquor ratio of 1:20, centrifuging and developing in a solution of Fast Blue Balt BB (3%) to which an addition of Diazopon A (1%) had been made. The material was washed thoroughly in cold water and dried. The yarn was divided into 10 g. lots and given an after-treatment for 15 minutes at the boil with the various auxiliaries, the concentration of which was maintained at 0.5% in every case. The results are indicated in Table III.

Table III/

Table III

Experiment	Name of auxiliary used	Rubbing fastness grade
1	Sodium myristate	2
2	" linoleate	2-3
3	" palmitate	1-2
4	" stearate	2
5	" laurate	2-3
6	" oleate	2-3
7	" anacardate	3
8	" tetrahydroanacardate	3
9	Igepal C	4
10	Igepon T	3
11	Nekal BX	3
12	Gardinol WA	3
13	Aerosol OT	3-4
14	Trisodium phosphate	4
15	Soap	3
16	0.5% soap 0.5% trisodium phosphate	3

Among the detergents examined Igepal C, trisodium phosphate, Aerosol OT come in for consideration in the diminishing order of rubbing fastness grade, followed by Nekal BX, Gardinol WA, sodium anacardate and tetrahydroanacardate, soap and a mixture of soap and trisodium phosphate. The sodium salts of the fatty acids occupy a slightly lower grade with the advantage in favour of the unsaturated derivatives such as the sodium linoleate and sodium laurate. Curiously enough it would appear that it is more the emulsifying and wetting agents such as Aerosol, Igepal and sodium phosphate (the latter has been claimed to have power to lower interfacial tension and marked power of emulsifying oils by Snell, Ind. Eng. Chem., 1931, 23, 470) that have led to increased resistance to rubbing rather than the well known detergents such as Igepon T, Gardinol WA and soap; testifying to the fact that for increased resistance to rubbing, the after-treatment should be done preferably with auxiliaries combining wetting and emulsifying action. Quite interesting though of slightly lower grade are the figures obtained in the case of the sodium salts of anacardic and tetrahydroanacardic acids whose efficiency may be ascribed partly to solubilisation in view of the structural similarity to Naphtol AS (though containing only one benzene ring) with a hydroxyl ortho to the carboxyl and with the added advantage of a long aliphatic chain.

Effect of after-treatment with auxiliaries of similar structure: In view of Hartley's theory (*loc. cit.*) about the tendency of organic compounds to dissolve in compounds of similar structure, six dyeings obtained from naphthols having long aliphatic residues such as N-2-hydroxy-3-naphthoyl-N'-oleyl-*p*-phenylenediamine, its meta isomer and N-2-hydroxy-3-naphthoyl-N'-caprylyl-*p*-phenylenediamine, by coupling 1% impregnations of these on bleached single 20's yarn, with 3% solutions of Fast Red Salt TR and Blue Salt BB respectively, have been submitted to an aftertreatment at boil for 15 minutes using 0.5% solutions of sodium salt of oleic and caprylic acids, washed, dried and the rubbing estimated. The results are recorded in Table IV. For purposes of comparison the rubbing fastness grades obtained by giving the respective dyeings a soaping after-treatment with 0.8% soap solution have been included. The results indicate the favourable effect of the after-treatment with auxiliaries of similar structure.

Table IV/

Table IV

Experiment No.	Naphthol	% auxiliary used	Rubbing fastness grade Fast Red Salt TR	 Fast Blue Salt BB
1	N-2-Hydroxy-3-naphthoyl-N'-caprylyl-*p*-phenylenediamine	0.8~~0~~ Soap	4-5	4-5
2	" "	0.5 Sodium salt of caprylic acid	5	5
3	N-2-Hydroxy-3-naphthoyl-N'-oleyl-*p*-phenylenediamine	0.8 Soap	4-5	4-5
4	" "	0.5 Sodium salt of oleic acid	5-6	5-6
5	N-2-Hydroxy-3-naphthoyl-N'-oleyl-*m*-phenylenediamine	0.8 Soap	4	3
6	" "	0.5 Sodium salt of oleic acid	5	5

Although in view of the limited range of naphthols dealt with, no conclusions of a general nature could be drawn, it would appear that the results obtained justify the assumptions of Hartley as regards the tendency of organic compounds to dissolve in compounds of similar structure, the better fastness exhibited by the dyeing after the special after-treatment ~~being~~ incapable of being explained other than as ~~a~~ due to a process of solubilisation and removal of the surface pigment by emulsification. The improvement effected, except in the case of 6 is not of a striking character, but if it is remembered that the dyeings from these naphthols exhibited even initially good resistance to ~~resistance~~ to rubbing, the higher figure obtained in the cases under discussion is significant.

Part V

Coupling of silk with diazo salts

INTRODUCTION

Among the textile fibres silk and wool rank as next in importance to cotton. While the principles underlying the processing of cotton are well understood and have been more or less systematised, the handling of the animal fibres in dyeing and related processes calls for careful manipulation in view of their structural characteristics.

Dyeing on silk is mainly carried out using acid colours, generally in a boiled-off liquor bath broken with sulphuric, formic or acetic acid, near the boil (90-95°C.) the period of dyeing varying from 1 to 1.5 hour. Though the colours dye level, the high temperature employed leads to a certain diminution in the natural lustre of silk which is attempted to be restored, partly at any rate, by treating finally in acidulated water. Fastness of these dyeings vary considerably, fastness to light being more or less mediocre while that to washing is generally satisfactory.

Attempts at using colours of the Naphtol AS range have met with limited success and are restricted in scope due to the high alkalinity of the Naphtol baths with consequent danger of deterioration of the fabric. The shades obtained, however, are characterised by excellent fastness to light and washing, but of inferior fastness to rubbing. The inferior rubbing fastness is partly due to the stronger Naphtol baths, large addition of salt and longer period of impregnation employed in view of the silk fibre exhibiting poor affinity for the Naphtols. Vat colours are used to a small extent mainly in yarn to form effect threads in dress goods and shirtings. According to Keyworth (J. Soc. Dyers Col, 1933, 49, 246) the affinity of most vat dyes for silk is so low that the production of dark shades becomes expensive. Proprietary agents added to the dye bath with a view to maintain the strength and lustre of the fabric, lead to a further diminution in the dyestuff absorption.

Diazo compounds are known to combine with proteins both by virtue of the phenolic hydroxyl group present in structural units of the tyrosine family, and the indole in the tryptophane units. Many of the chemical and physical properties of a protein are intimately related to the number and arrangement of its functional or reaction groups most of which are contributed by the dibasic and diacidic amino acids. Silk fibroin is composed largely of the amino acids glycine, alanine and tyrosine and of these only the last one would be expected to contribute a reaction group namely, a phenolic hydroxyl. It is this reactive group which decides largely the absorption of moisture, acids and dyes. This has been conclusively proved by various investigators who inactivated these groups with a veiw to study the properties of the modified proteins.

Advantages due to the presence of these groups appear to have been utilised in the French "Escaich process" in which the silk is dyed in a bath containing an organic acid, a metallic salt and a nitrite to produce shades of yellow, garnet and green, the metallic salts used being those of aluminium, copper, nickel, cobalt and iron. It is claimed that the colours are obtained in a short time with a cold bath and could be made resistant to washing and light.

In an attempt at studying the constitution of the azo compounds of the silk fibres, Morel and Sisley (Bull. Soc. Chim., 1927, 41, 1217-24) suggested that the colourations obtained by diazotising and coupling on the fibres are due to the formation of coloured azo compounds from the tyrosinic grouping in the fibre. They found that if the diazo compound so obtained was reduced with stannous chloride or sodium hydrosulphite, ~~wh~~ an amino group was substituted for the diazo group, which reacted rapidly with nitrous acid to give the same coloured bodies as obtained by treating the fibre for long periods with an excess of nitrous acid. Sisley, Simonnet and Sisley (Bull. Soc., Chim., 1930, 47, 1389-94) coupled diazotised solutions of bases of the type of dichloraniline, nitroanisidine and dianisidine and obtained ~~impo~~ shades ranging from yellow to brown of industrial importance. They observed that silk, in addition to the dye formed by coupling with the fibre, held a certain amount of the non-coupled diazo compound, which on boiling with soap formed a hydroxy derivative, which in turn coupled with the unchanged diazo compound to give a complex absorbed on the silk. Thus silk dyed in diazotised primuline and boiled in soap gave a fast yellow, since the diazo compound of primuline is stable and it is the azofibroin azoprimuline dye, which predominates. According to these authors the azo dyes formed by coupling a diazo compound with the tyrosine group of fibroin are comparable in shade and reactions with dyes such as *p*-nitrobenzeneazo-*p*-cresol, the differences noticed in fastness to scouring being attributable to the large protein molecule.

According to *E.P.* 437,049 wool or silk dyeings obtained with diazo compounds became deeper in colour and/or their fastness properties are improved by subsequent treatment with metallic salt solutions. Sodium bichromate-sulphuric acid mixture is particularly effective in the case of shades obtained with the acid of α- and β-naphthyldiazonium chlorides, whilst neutral or acid (acetic) solutions of copper salts are effective with dyeings produced with diazo salts of negatively substituted anisidines. The colours obtained vary from deep brown to reddish brown.

o- Amino-
phenol- S
of 1-NH_2- 2-
nl- 4- S

The utilisation of this coupling reaction between silk and diazo compounds for industrial purposes appears, however, not to have been attempted, probably due to the lack of quantitative data on the fastness properties of the resultant shades and inadequate information as to the range of shades available. It has now been found that this reaction could be utilised to produce shades ranging from a wide variety of yellows, golden yellows, oranges, browns, maroons and chocolate. Some of the shades produced compare very favourably with basic colours in brightness while excelling them in fastness to light and washing. Since the coupling is effected at room temperature (30°C.), problems such as loss of lustre due to high temperature are eliminated, and as the period of dyeing is nearly the same as in the case of acid dyestuffs, the process should be capable of large scale application, particularly with regard to the limited range of shades mentioned in the experimental part.

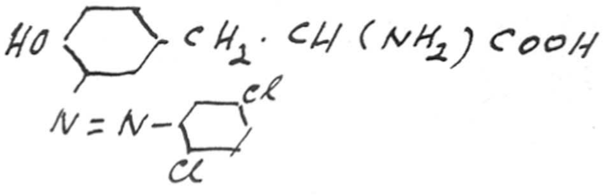
The influence of buffers in coupling has been studied. Buffers play a vital part in not only hastening the coupling reaction but lead~~s~~ to a decided improvement in the depth of and fastness properties of the resultant shades themselves. Certain groupings in the diazo compounds also appear to influence the coupling to a considerable extent. Negative substituents led generally to deep shades of good fastness to light and washing.

Generalisations as regards the ability of certain substituent~~s~~ groups to favourably influence the fastness to light in the case of dyes of the azoic class do not appear to find a parallel here. One of the groupings that is claimed to influence the light fastness of the azoic dyeing is the methoxy or ethoxy groups. But in the case of the dyed shades on silk it has been found that this grouping does not appear to be a useful factor as far as fastness to light is concerned.

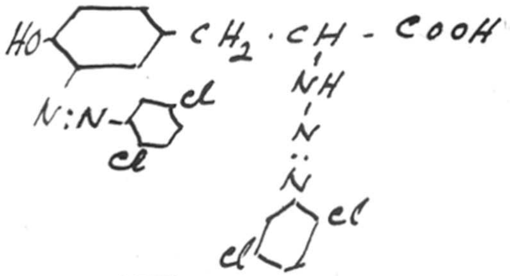
One possible use to which this coupling reaction could be utilised is in the production of two-tone effect on union fabrics. Attractive dyeings have been obtained by using cotton silk unions, in which the cotton is left practically unstained. The extension of the scope of this reaction for the estimation of the relative amounts of the fibres composing the union is under investigation.

Silk has been dyed with acid, basic and direct dyes containing an exo-amino group and the amino groups diazotised and allowed to couple with the phenolic constituent of the silk fibroin. In this way starting with relatively loose shades, faster and better dyeings have been produced.

To study the mechanism of the reaction, L-Tyrosin (Theodore Schuchardt's product) has been coupled with diazotised 2:5-dichloraniline using 1 and 2 mols. to produce compounds I and II



(I)



(II)

Attempts at preparing the N-benzoyl derivative of compound (II) proved a failure, showing thereby that the second position occupied by the diazo component was ~~a~~ on the primary amine.

Aniline dye
Mono- & dibenzoyl derivs

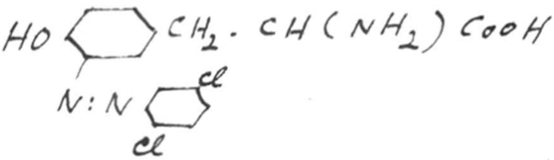
~~EX~~

EXPERIMENTAL

Monazo dye from L-tyrosine and 2:5-dichloraniline:

Couple N-benzoyl tyrosine

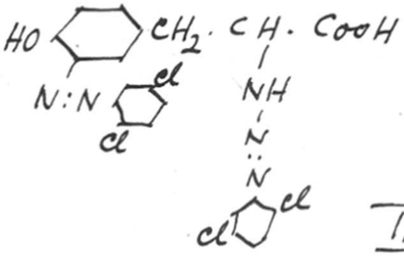
Benzoylate ←



(I)

L-Tyrosine (1 g.) (1 mol.) was taken up in alcohol (5 c.c.) and water (25 c.c.); to this was added caustic soda 32.5% (1 c.c.) and stirred. To the resultant solution diazotised 2:5-dichloraniline (1 g.) (1.1 mol.) was added. A bright orange dye was obtained which gradually changed to brownish orange. The dye (1.4 g.) was crystallised from acetic acid in pale yellow brown crystalline powder melting at 118-120°C. (Found: Cl, 20.0. $C_{15}H_{13}O_3N_3Cl_2$ requires Cl, 20.0%).

Disazo dye from L-tyrosine and 2:5-dichloraniline:



II

Diazotised 2:5-dichloraniline (2 g.) (2.2 mols.) was added to L-tyrosine (1 g.) dissolved as above. The resultant dye crystallised from acetic acid in yellow brown plates which melted at 183-5°C. (Found: Cl, 26.8. $C_{21}H_{15}O_3N_5Cl_4$ requires Cl, 26.9%).

Attempts at preparation of the N-benzoyl derivative of compound II proved a failure, the resulting product gi giving a melting point 183-85°C., which is the same as that of compound II, showing thereby that the coupling had taken place at the amino group.

To study the effect of buffers in coupling, a series of diazo salts and diazotised amines have been allowed to react with silk, a 2% concentration of diazo salts and sodium acetate were employed, the time of impregnation being 1 hour at room temperature (30°C.). The dyeings were washed in cold water and dried. In Table I is recorded observations as regards the constitution of the diazo compound and the shades obtained with and without sodium acetate. In naming the shades, use has been made of the British Colour Council Dictionary of Colour Standards, 1934. It was noticed that the buffer invariably led to increased depth in shade and in quite a large number of cases the shades were entirely different even in tone from those obtained from non-buffered solutions. In a few cases, as for instance, in the complex diazo salts of the type Variamine Blue FG, B and Violet B, while the buffer exerted the same beneficial influence, the differance between the shades obtained from the buffered and non-buffered solutions was not so pronounced as in the case of simpler types of diazo components such as Fast Yellow Salt GC (o-chloraniline) or Fast Orange Salt GR (o-nitraniline), while in a smaller number of cases such as Fast Red Salt TR (5-chloro-2-aminotoluene) and Fast Red Salt RC (4-chloro-2-aminoanisole) the shades obtained from diazo baths containing no buffer were extremely poor in tinctorial value.

Table I

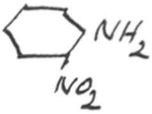
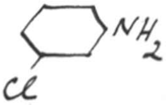
Fast colour Salt or Base	Constitution of the Salt or Base	Shade	
		With sod. acetate	Without sodium acetate
Fast Yellow Salt GC		Butter cup	Straw
Fast Orange Salt GR		Marigold	Golden orange
Fast Orange Salt RD	—	Indian yellow	Butter cup slightly redder
Fast Orange Salt GC		Lemon	Straw

Table I contd.

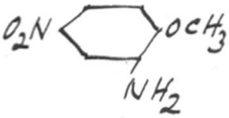
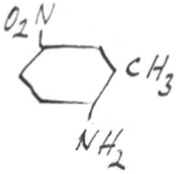
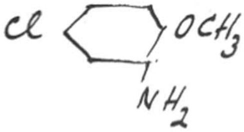
Fast colour Salt or Base	Constitution of Salt or Base	Shade	
		With sod. acetate	Without sodium acetate
Fast Orange Salt GCD	—	Deep butter cup	Light butter cup
Fast Scarlet Salt R		Saffron	Light lemon
Fast Red Salt RL		Reddish orange	Saffron
Fast Red Salt RC		Saffron	Champagne

Table I contd.

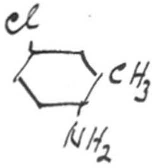
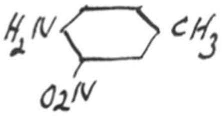
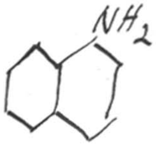
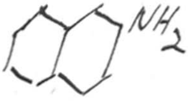
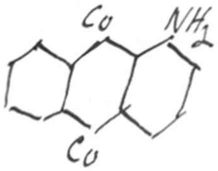
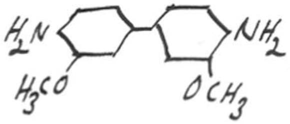
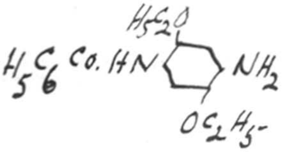
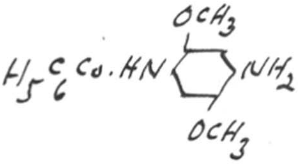
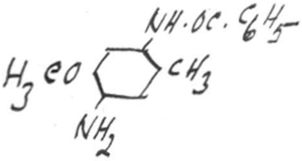
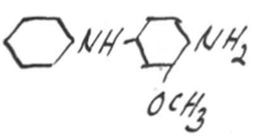
Fast colour Salt or Base	Constitution of Salt or Base	Shade	
		With sod. acetate	Without sodium acetate
Fast Red Salt TR		Straw	Champagne
Fast Red Salt FG	—	Deep golden orange	Butter cup
Fast Red Salt GL		Copper brown	Pale brown
α -Naphthylamine		Nutmeg	-
β - "		Terra cotta	-
Red Salt AL		Ruby	Rust

Table I contd

Fast colour Salt or Base	Constitution of Salt or Base	Shade	
		With sod acetate	Without sodium acetate
Blue Salt B		Copper brown	Light mace
Blue Salt BB		Golden brown	" "
Blue Salt RR		Deep rust	Deep cinnamon
Violet B		Mastic	Light olive brown
Variamine Blue B		Mastic	Light olive brown
Variamine Blue FG		Rose beige	Pink beige

Addition of a buffer in the form of sodium acetate led invariably to increase in depth of shade. It was therefore considered desirable to study the action of other buffers such as sodium carbonate bicarbonate, trisodium phosphate, disodium hydrogen phosphate and sodium hexameta phosphate. The coupling was effected at room temperature (30°C.) using Fast Scarlet Salt GG (2:5-dichloraniline) (2% on volume) for 1 hour the concentration of buffer being 1% on volume. In all the cases the solutions were cloudy and there was a certain amount of precipitation. Table II indicates the results obtained, the buffers being arranged based on decreasing order of clarity of the diazo baths.

Table II

No.	Buffer used	Nature of solution obtained	Shade
I	Sodium acetate	Clear	Deep golden yellow
II	Trisodium phosphate	Olive colour precipitate	Indian yellow slightly light
III	Disodiumhydrogen phosphate	Brown precipitate	Buttercup, slightly weaker and duller
IV	Sodium hexametaphosphate	Colourless precipitate	Lemon
V	Sodium bicarbonate	Heavy creamy precipitate	Saffron
VI	Sodium carbonate	Very heavy olive coloured precipitate	Tangerine, slightly browner

The shades obtained arranged in decreasing order of depth would be (VI), (V), (I), (II), (III) & (IV). But the dyeings from (VI) and (V) had a slight brownish tinge and lacked the bloom characteristic of sample I. Any advantage of increased depth in cases of (V) and (VI) is more or less nullified by the heavy precipitation which tended to ~~given~~ give uneven results.

Fastness to light and washing: All the dyeings mentioned in Table I were tested for fastness towards light and washing. Light fastness was determined by methods described by Bhat and Ramachandran (J. Ind. Chem. Soc., Indl. Ed., 1942, 5, 11) and fastness to washing according to the specifications contained in the Report of the "Echtheintokommission" (the Fastness Committee appointed by the Society of German Chemists in 1911) in which the dyeing is plaited with the same quantity (by weight) of silk, and treated for 1/4 hour at 40°C. with 5 g./litre Marseilles soap (free from caustic alkali) in a material liquor ratio of 1:50. The plait being then dipped 10 times into the liquor, and after each dipping wrung thoroughly by hand, well squeezed, rinsed in cold water and dried. The samples were then graded on the basis of bleeding in the bath and loss of depth on the dyed sample.

Table III

Fast colour Salt or Base	Change in shade on washing		Fastness grade			
			Light		Washing	
	With sodium acetate	Without sodium acetate	With sodium acetate	Without sod. acetate	With sodium acetate	Without sod. acetate
Fast Yellow Salt GC	Slightly weaker than original	Weaker than original	2-3	2-3	4-5	3-4
Fast Orange Salt GR	Deeper and redder than original	Slightly deeper than original	2-3	3	5	5
Fast Orange Salt RD	"	"	2-3	2-3	5	5
Fast Orange Salt GC	Practically no change in shade	Distinctly weaker than original	6-7	2-3	5	2-3
Fast Orange Salt GCD	Deeper and slightly greener than original	Deeper and redder than original	6-7	6-7	4-5	4-5
Fast Scarlet Salt R	Nearly unchanged	Slightly weaker	6-7	2-3	5	5
Fast Red Salt RL	Deeper than original	Slightly deeper and redder	6-7	2-3	5	5
Fast Red Salt RC	No change	"	2-3	2-3	5	5
Fast Red Salt TR	Slightly weaker	Slightly weaker	2-3	2-3	4	4

Table III contd.

Fast colour Salt or Base	Change in shade on washing		Fastness grade			
			Light		Washing	
	With sodium acetate	Without sod. acetate	With sodium acetate	Without sod. acetate	With sodium acetate	Without sod. acetate
Fast Red Salt FG	Deeper and brighter	Deeper and slightly redder	3-4	2-3	5	5
Fast Red Salt AL	"	Slightly deeper and browner	6-7	3-4	5	4-5
Fast Blue Salt B	"	Slightly weaker	1	1	5	4-5
Fast Blue Salt RR	Same as original	Slightly browner than original	1-2	1-2	5	4
Fast Blue Salt BB	"	Slightly weaker	1-2	1-2	5	3-4
Fast Variamine Blue B	Slightly browner	" "	1-2	1-2	4	4

? Pres~~sure~~ence of methoxy, nitro and chlorine groups in the diazo compounds would appear to be an advantage as far as light fastness is concerned. The shades obtained from Fast Orange Salt GC (m-chloraniline), Fast Scarlet Salt R (4-nitro-2-aminoanisole) and Fast Red Salt RL (5-nitro-2-aminotoluene) by buffering with sodium acetate are characterised by good fastness to light. Probably the position of these groups in the nucleus is an important factor; Fast Yellow GC (o-chloraniline) exhibited only moderate fastness to light, while Fast Orange GC (m-chloraniline) was of very good fastness to light. All the complex amines represented by Blue Salts RR, BB and Variamine Blue B gave poor shades of inferior fastness to light and of medium fastness to washing. They are unsuitable to be used as coupling components in the case of silk.

The increased depth of shade noticeable on treating the dyed fabrics with soap solutions could be explained by the observation made by Sisley, Simmonnet and Sisley (loc. cit.) that silk holds a certain amount of diazo compound in a non-coupled form which on boiling with soap is transformed into a hydroxy derivative, the latter coupling with the unchanged diazo compound to give a complex absorbed on the fibre.

In view of the possibility of getting increased fastness by incorporating metallic radicles in dyeings obtained with diazo salts (cf. B.P. 437,049, loc. cit.) coupling has been effected between silk and Fast Yellow Salt GC (2% on volume) in the presence of sodium acetate (2%) to which additions such as ferrous acetate chromium acetate and aluminium sulphate respectively were made, the time allowed for coupling being 15 minutes. The materialswere taken out evenly squeezed, dried and steamed in the steaming cottage 15 minutes without pressure and washed. The three samples differed in shade from one another. Their fastness to light and washing were examined and are enumerated in Table IV.

Table IV/

Table IV

Mordant used	Per cent mordant used	Shade	Fastness	
			Light	Washing
Aluminium sulphate	1	Lemon	1	3-4
Ferrous acetate	3	Satinwood	1	3-4
Chromium acetate	2	Buttercup	1	4

It would appear that in the case of Fast Yellow Salt GC at any rate the effect of addition of a metallic salt did not lead to any improved fastness to light, while the fastness to washing remained more or less the same as in the case of where no mordant was employed (cf. Table III).

Silk cotton union fabrics (6" x 6" and weighing 2 g.) were treated with solutions (2.5% on volume) of Fast Red Salt RC and Fast Blue Salt B respectively each containing sodium acetate (8% on volume). The impregnation was carried out. For a period of 1 1/2 hour and at the end of the period the samples were removed, washed and soaped for 15 minutes at 45°C. In the case where the coupling had been effected with Fast Blue B the shade of "Murrey" produced on silk in the presence of undyed cotton gave an attractive lustrous effect, which could only be imitated by weaving. Similar effect was obtained in the case of Fast Red RC, the shade obtained being different.

With a view to investigating the possibility of using this coupling reaction for improving the fastness properties of dyed shades on silk with dyes containing a free amino group, diazotising this group and allowing it to couple with the tyrosine.

For purposes of experiment two dyes were chosen, viz. Chicago Blue RW and Cloth Red 3G. Silk (10 g.) was dyed a 3% shade of each of the above dyestuffs, the dyeing being carried at 85°C. for 45 minutes, using a material liquor ratio of 1:30, the pieces rinsed in cold water and dried at room temperature (30°C.).

A cutting from each of the above samples weighing about 4.25 g. was suspended in a beaker of cold water (100 c.c.) containing enough ice to give a final volume of 200 c.c.; the beaker was kept in freezing mixture, care being taken to keep the temperature at about 2°C. To the water concentrated hydrochloric acid (10 c.c.) was added, followed by an addition of sodium nitrite solution (15%, 10 c.c.) from a pipette, the nozzle of which was kept immersed below the surface of liquor in the beaker.

Diazotisation of the dye on the fibre was allowed to proceed for 15 minutes. At the end of the period sodium acetate (20 g.) was added to the solution in the beaker to neutralise the mineral acidity and thus allow coupling to take place between the phenolic hydroxyl of the tyrosine and the diazo compound from the respective dyes on the fibre. At the end of 1 hour the material was taken out rinsed and dried. The change in shade observed during and at the end of the process are given in Table V.

Table V

Dyestuff taken	Original shade on silk	Shade after diazotisation	Final shade
1. Chicago Blue RW	Sapphire	Lido	Deeper lido
2. Cloth Red 3G	Cherry	Beetroot	Guardsman Red

To confirm that the alteration in the shade obtained was due to diazotisation and coupling, undyed silk (5 g.) was introduced into a solution of Chicago Blue RW (0.15 g.) diazotised in exactly the same manner as before and kept immersed for a period of 1 hour, washed and dried. It was noticed that the resultant shade was identical with the final shade obtained above, although slightly weaker in depth.

The samples were subjected to a soaping test, this being carried out according to the specification of the German Fastness Committee (<u>loc. cit.</u>). The results are indicated in Table VI.

Table VI

Dyestuff used	Soaping fastness grade	
	Original	Diazotised and coupled
Chicago Blue RW	3	4-5
Cloth Red 3G	2-3	3-4

In both the cases the coupling reaction led to increased fastness to soaping. In view of the large number of substantive and other dyes available with free diazotisable amino groups, this reaction should prove useful in getting shades of better fastness.

The following publications of the author are submitted as supplementary evidence.

1. Studies in the Naphtol AS series. Fastness to rubbing (*J. Soc. Dyers Col*., 1938, **54**, 209).
2. The seed husk of *Plantago ovata* in printing and finishing (*J. Soc. Dyers Col*., 1938, **54**, 462)
3. Cutch - Part I. Modified shades by coupling with diazo salts (*J. Soc. Dyers Col*., 1938, **54**, 513).
4. Wetting agents in textile processing. Part III. Calcium soap dispersing power (*J. Soc. Dyers Col.*, 1938, **54**, 520).
5. Trisodium phosphate as a textile auxiliary. Part I. Properties as a kier-boiling assistant, *J. Ind. Chem. Soc., Indl. Ed.*, 1939, **2**, 81).
6. Some experiments in light fastness (*J. Ind. Chem. Soc., Indl. Ed.*, 1942, **5**, 11).
7. Processes for applying cutch in dyeing and printing (*Indian Patent N*o. 24056/1937)
8. Khaki and allied shades from cutch on textile fibres (*Indian Patent N*o. 26980/1939)
9. Studies in the Naphtol AS series. Part VI. Synthetical experiments III. Synthesis of Naphthols ~~l~~with~~e~~ paraffin chains (*J. Soc. Dyers Col*., 1942, **58**, 203).

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 reference to the literature on the subjects on which the present work is based, have been mentioned in the introductory parts of this thesis. General guidance has been received from Dr. K. Venkataraman, D.Sc., 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.

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