CHAPTER 3

RESULTS AND DISCUSSION

3. RESULTS AND DISCUSSION

3.1. INTRODUCTION

Certain fastness properties of reactive dyeings are governed by the reactive system. A reactive dyeing must exhibit a certain minimum stability to alkaline and acid hydrolysis for the commercial interest. The stability required depends on the intended use of the dyed material.

Furthermore, the resistance of a reactive dyeing to alkali has to be correlated with the reactivity of the dyestuff. All the reactive dyes are known so far, must be fixed on cellulose in alkaline medium. Hence it is possible that during the course of fixation a part of the dye which has already reacted with the fibre may be hydrolyzed.. The prerequisite for a reactive dye that can be used under alkaline fixing conditions is that the rate of hydrolysis of the dyeing under the fixing conditions must be negligible in comparison to the rate of fixation..

The stability of reactive dyeings to acid hydrolysis is also of great practical importance. Most dyed cellulose fabrics receive a resin finish, which is applied with an acid catalyst. Furthermore, the acidic atmosphere prevalent in many industrial areas is likely to attack reactive dyeings that are easily hydrolyzable. Even when such acid hydrolysis proceeds very slowly, definite deterioration of the dyed goods may be observed after long storage. With the growing use of blended fabrics of cellulose and synthetic fibres, the fastness of the dyed cellulose component to acid-cross-dyeing is of increasing importance.

The study of the sensitivity of the dyeings of reactive dyes to alkali and acid hydrolysis and of the fixation rate of the corresponding dyestuff has been done by Benz et. al. (1,2). The bridging system is affecting the reactivity of the dye to a great extent and the tendency of the corresponding dyeing to hydrolyze. The imino bridging system is easily undergoing to acid hydrolysis while oxygen bridging system is susceptible to alkaline hydrolysis. With a view to synthesize reactive dyes having a bridging system unaffected to acid or alkaline hydrolysis, in the present investigation reactive dyes possessing -C-C- bridging system have been synthesised.

3.2 REACTIVE COUPLING COMPONENTS

Three reactive coupling components having -C-C- bridging system are synthesised by Friedel-Crafts reaction. Price has defined the Friedel-Crafts reaction as " a Process of uniting two or more organic molecules through the formation of carbon to carbon bonds under influence of certain strongly acidic halide catalysts such as aluminium chloride, boron trifluoride, ferric chloride, zinc chloride etc. ......", (3). In general sense, today we consider Friedel-Crafts type reaction to be any substitution, isomerisation, elimination, cracking, polymerisation, or addition reactions taking place under the catalytic effect of Lewis acid type acidic halides or proton acids. The different aspects of Friedel-Crafts reaction is well covered by Olah (4).

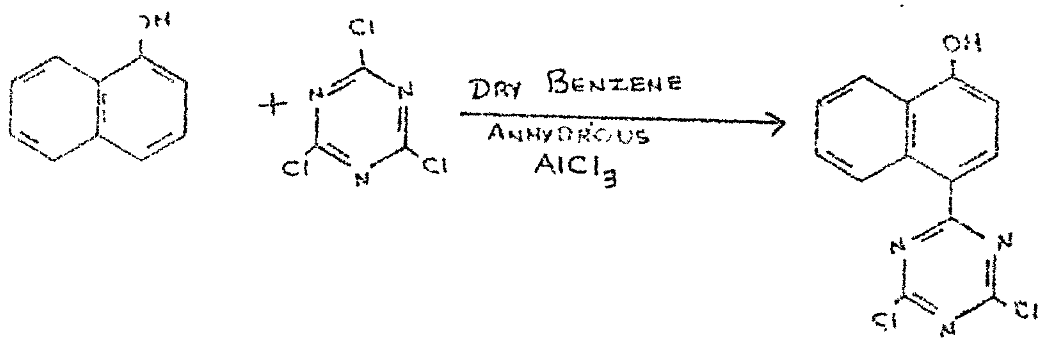
The capacity of cyanuric chloride - 2,4,6 - trichloro-s-triazine-undergoing Friedel-Crafts reaction with 1-naphthol was long been realized (5). But not any reactive dye was prepared by this method, till 1962 when ICI and General Aniline and Film Corporation claimed reactive dyes prepared by Friedel-Crafts method (6-8). In the present investigation, cyanuric chloride was reacted with 1-naphthol and 1-anthracenol in presence of anhydrous aluminium chloride. While the reaction between cyanuric chloride and 8-hydroxy quinoline was carried out without any catalyst. The general reaction route is shown in Scheme-1.

When the reaction between cyanuric chloride and 8-hydroxy quinoline was carried out in presence of anhydrous aluminium chloride, the product obtained after decomposing aluminium chloride complex with dil HCl was in 10% yield. When the aluminium chloride complex was decomposed with acetic acid, the yield was increased from 10% to 20%, and when the reaction was carried our without catalyst, 40% yield was obtained. The reason for this type of behaviour is still not clear.

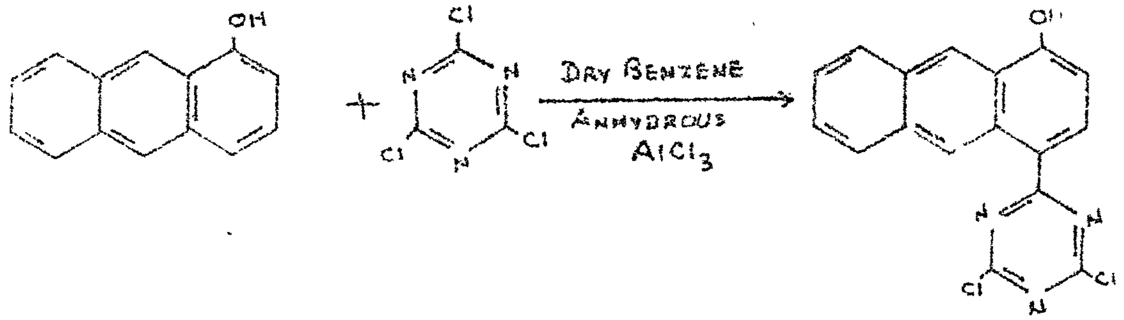
All the three reactive coupling components, 2,4-dichoro-6-(4'-hydroxy-1'-naphthyl)-s-triazine(reactive naphthol); 2,4-dichloro-6-(4'hydroxy-1'-anthracenyl)-s-triazine (reactive anthracenol) and 2,4-dichloro-6-(8'-hydroxy-5'-quinolinyl)-s-triazine (reactive 8-hydroxy quinoline) were analysed for their C, H and N content. They are given in Table-1. The percentage

SCHEME - 1

① 2,4 - DICHLORO - 6 - (4'- HYDROXY - 1'- NAPTHYL) - S - TRIAZINE



② 2,4 - DICHLORO - 6 - (4'- HYDROXY - 1'- ANTHRALENYL) - S - TRIAZINE



③ 2,4 - DICHLORO - 6 - (8'- HYDROXY - 5'- QUINOLINYL) - S - TRIAZINE

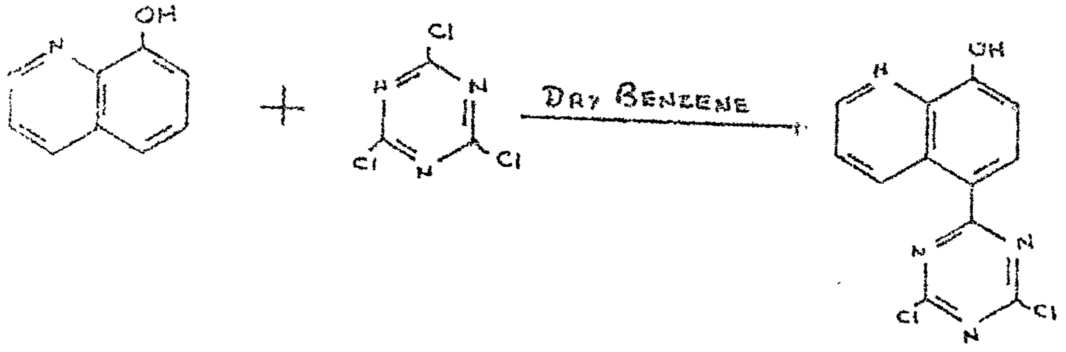


TABLE 1

Melting Point and Elemental Analysis of Reactive Coupling Components

No.	Reactive Coupling Component	Mol.Formula	M.P. °C	Elemental Analysis					
				Found			Calculated		
				% C	% H	%N	% C	%H	% N
1	Reactive naphthol	$C_{13}H_7N_3Cl_2O$	225	53.77	2.148	14.60	53.42	2.397	14.38
2	Reactive anthrocenol	$C_{17}H_9N_3Cl_2O$	>300	65.19	2.431	9.967	65.67	2.238	10.44
3	Reactive 8-Hydroxyquinoline	$C_{12}H_6N_4Cl_2O$	185	49.42	2.36	18.72	49.15	2.047	19.11

found are in good agreement with the calculated one.

3.3 U.V. AND IR SPECTRA OF REACTIVE COUPLING COMPONENTS

The spectra characteristic of the reactive coupling components are given in Table 2. The representative IR spectra is shown in Fig 1 and U.V. spectra is shown in Fig 2.

The infrared spectra of the reactive coupling components are mainly discussed for their characterisation. The predominent stretching vibrations are discussed.

Generally the free hydroxyl group of alcohols and phenols absorbs strongly in 3650-3584 cm^{-1} region (9). In the present investigation the peaks around 3500 cm^{-1} in compounds 1 and 2 are assigned at free phenolic OH stretching vibrations, while the compound 3 is having the hydroxyl stretching vibration at 3300-3100 cm^{-1}. The lower shift is due to the intra molecular hydrogen bonding of the chelate type (10).

The spectra of s-triazine shows absorption in three main regions 1550 cm^{-1} (quadrant stretching), 1420 cm^{-1} (semi circle stretching) and 800 cm^{-1} (out of plane ring bending by sextants) (11-14). In the compounds 1 to 3

TABLE 2

U.V. and I.R. Spectra of Reactive Coupling Components

No.	Reactive Coupling component	U.V. maxima in nm (methanol)	Characteristic Infrared Frequencies in cm^{-1}				
1	Reactive Naphthol	241	3500	1580	1460	820	800
2	Reactive Anthracenol	274	3450	1560	1450	830	790
3	Reactive 8-hydroxy quinoline	235,310	3300-3100	1540	1450	810	790

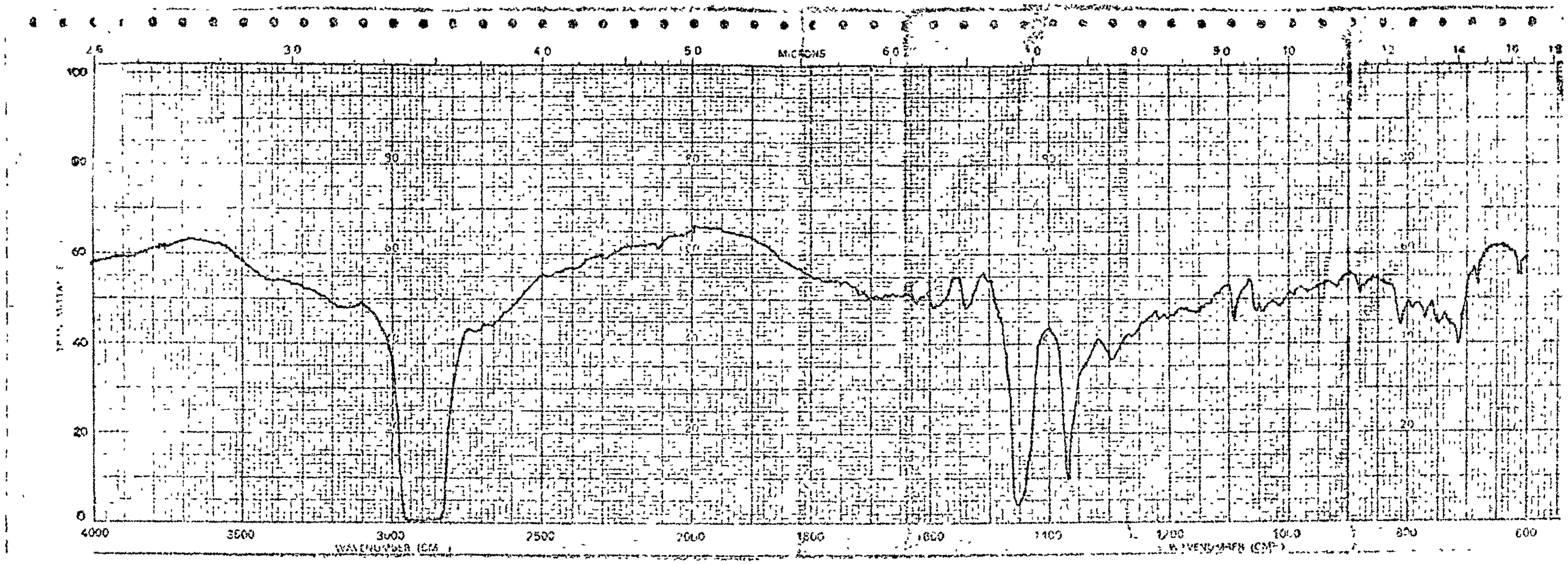


Fig.1 IR spectra of reactive 8-hydroxy quinoline in nujol mull.

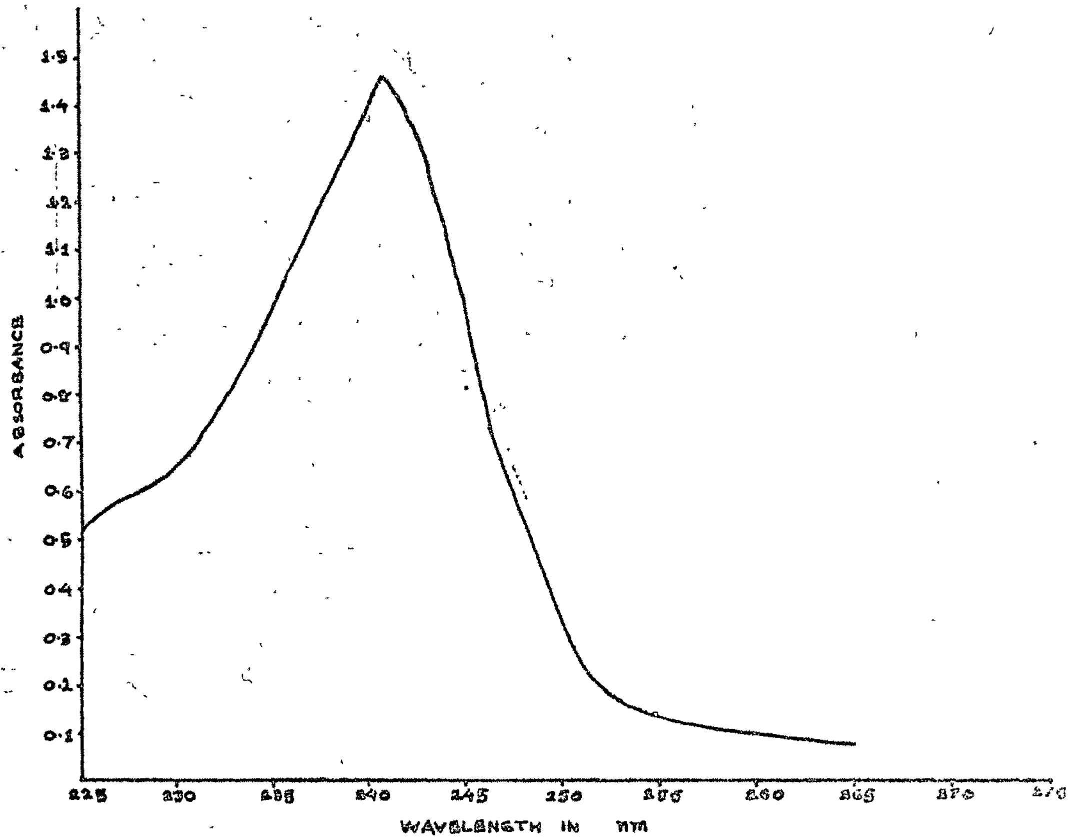


Fig.2 U.V. spectra of reactive 8-hydroxy quinoline

these bands are observed in the regions 1580-1540 cm^{-1}, 1460-1450 cm^{-1} and 800-790 cm^{-1}, which are in confirmity of the reported by others (15,16).

The substitution of chlorine atom into 2 and 4 position of the s-triazine absorbes in the region of 850 cm^{-1} (15). This band is assigned in 830 cm^{-1} region.

The commonly accessible ultraviolet spectra of benzene, naphthalene and anthracene consist of three well defined main absorption bands, all due to $\pi-\pi^*$ transitions (17,18). These bands are designated as bands I, II and III (18).

	Band I nm	Band II nm	Band III nm
Benzene	183	207	225
Naphthalene	220	275	312
Anthracene	225	379	-

Substitution on these rings does not usually produce great changes or new bands in the spectra, but only modifies the spectrum of the parent compound. In the present investigation the reactive coupling components are basically derived from naphthalene ring and the λ max are in order of

Compound No. $2 > 1 > 3$

λ max $274 > 241 > 235$

The introduction of a fused ring into naphthalene gives a bathochromic shift viz. naphthalene to anthracene. Similarly the compound 2 is having a bathochromic shift as compared to compound 1. Generally the heterocyclic compounds are having the $n \rightarrow \sigma^*$ transition and possess a lower shift as compared to benzene or naphthalene in the ultraviolet spectra (19). Similarly the compound 3, 8-hydroxy quinoline derivative have the lower shift as compared to the compound 1. Further these spectra are discussed on the basis that the s-triazine structure of the molecule is common in all the compounds and have the similar effect on the substitution in the ultraviolet region. More over the s-triazine absorbs at 222 nm in the ultraviolet region (19).

3.4 REACTIVE AZOIC DYEING OF COTTON AND WOOL

The insoluble azo dyes are formed on the fibre in two steps, by combination of a diazotised organic amine in solution with a naphthol, previously impregnated on to the textile material as the sodium salt. They have been variously called " ice colours", "azoics", and "ingrain colours", all terms, more or less are descriptive of their application on nature.

The introduction of Naphthol AS, the anilide of 3-hydroxy-2-naphthoic acid as azoic coupling component marked an important advance. The greatest utility in dyeing with Naphthols is in the deep shades of oranges, scarlets, reds, maroons, navy blues, browns, and blacks. The various aspects of azoic dyes has been dealt with in considerable details in many monographs (20-24) and in many text books (25-29).

Due to the fact that coloured pigment is built on the fibres as well as in part in developer bath, the dye can settle on the fibre purely mechanically. In such a case, the desired fastness of colouring is possible through proper precuations such as :

(a) rinsing of primary foundation with electrolyte containing dilute sodium hydroxide,

(b) adding proper dispersive agents in developing bath and

(c) by hot soap solution treatment of completed dyeing material.

Eventhough after taking such precautions, in certain cases the specific increase in quality may not always be reached.

In principle, one can overcome these difficulties, by bonding the naphthol covalently on the fibre, so that naphtholate foundation can be treated with hot soap solution for effective removal of unbonded naphthol before development, thus avoiding the azo pigment in the developer bath, forming a weak bonding. The colour developed in this manner posses improved washing, rubbing as well as pronounced solvent fastness. The important factor for such a highest fastness is naturally a total removal of non-covalently bonded naphthol before the coupling. In literature patents are claimed for the use of reactive naphthols (30-33). Broecker et al. have synthesized reactive naphthols and have tested as reactive azoic coupling components (34). It was therefore, thought of interest to study the synthesised reactive naphthol and reactive anthracenol in reactive azoic dyeing of cotton. The study has been extended for wool dyeing also. Since reactive 8-hydroxy-quinoline possess low solubility in alkali, it has not been evaluated for reactive azoic dyeing.

The reactive naphthol and reactive anthracenol were dissolved in aqueous sodium hydroxide for cotton dyeing and in aqueous sodium carbonate for wool dyeing. After impregnating the solution of reactive naphthol and reactive anthracenol on wetted hanks, hanks were developed in 3% neutral solution of diazotised base. The amines used for developing cotton fibres are listed in Tables 3 and 4, while for wool fibres are given in Tables 5 and 6.

3.4.1 Reactive Azoic Shades

The available naphthols are divided into two broad classes on the basis of the azoic shades.

(a) Naphthols which yield a series of shades according to the diazonium salt used for development and

(b) Speciality naphthols, which are so constituted that each yields more or less the same shade with any base or salt.

In the present case, both the reactive components, reactive naphthol and reactive anthracenol, come in the second class. The reactive naphthol gives orange to scarlet shades on

TABLE 3

Reactive Azoic Dyeing of Cotton with Reactive Naphthol Base, Colour and Fastness Properties

No.	Base	Colour	Washing Fastness		Light Fastness	Rubbing Fastness	
			Staining	Compare to Pattern		Wet	Dry
1	2	3	4	5	6	7	8
1	Aniline	Pink	5	4-5	6	3-4	4
2	o-Toluidine	Red	5	4-5	4-5	4	4
3	m-Toluidine	Red	5	5	4-5	4	3-4
4	p-Toluidine	Pink	5	4-5	4-5	4	3
5	o-Anisidine	Orange	5	5	5	4	4
6	p-Anisidine	Orange	5	5	5	4	4
7	o-Cl-aniline	Scarlet	5	5	4-5	3	3-4
8	m-Cl-aniline	Orange	5	4-5	4	3	3-4
9	p-Cl-aniline	Orange	5	4-5	4-5	4	4
10	o-Nitro-aniline	Red	5	4-5	4	4	4

TABLE 3 contd...

1	2	3	4	5	6	7	8
11.	m-Nitro-aniline	Orange	5	4-5	4	4	4
12.	p-Nitro-aniline	Orange	5	5	5	3-4	4
13.	p-Bromo-aniline	Red	5	5	5	4	4
14.	p-Fluoro-aniline	Orange	5	4-5	4	3-4	3-4
15.	p-Phenitidine	Red	5	4-5	4	4	3-4
16	5-Cl-2-Me-aniline	Orange	5	4-5	4-5	4	4
17	5-Nitro-2-Me-amiline	Reddish orange	5	4-5	6	4	4
18	5-Nitro-o-anisidine	Violet	5	4	6-7	4	4
19	a-Naphthylamine	Bourdex	5	4	4-5	3-4	3-4
20	B-Naphthylamine	Scarlet	5	4-5	6	4	3-4

TABLE 4

Reactive Azoic Dyeing of Cotton with Reactive Anthracenol Base, Colour, Fastness Properties.

No.	Base	Colour	Washing Fastness		Light Fastness	Rubbing Fastness	
			Staining	Compare to pattern		Wet	Dry
1	2	3	4	5	6	7	8
1.	Aniline	Light bourdex	5	5	5	4	4
2.	o-Toluidine	Brown	5	5	4	4	4
3.	m-Toluidine	Brown	5	5	4	4	3-4
4.	p-Toluidine	Light bourdex	5	5	4	4	3-4
5.	o-Anisidine	Brown	5	5	5	4	4
6.	p-Anisidine	Brown	5	5	5	4	4
7.	o-Chloroaniline	Scarlet	5	5	4	3-4	3-4
8.	m-Chloroaniline	Scarlet	5	5	4	3	3
9.	p-Chloroaniline	Brown	5	5	4	3-4	4
10.	o-Nitroaniline	Light bourdex	5	5	4	4	4

TABLE 4 (contd.)

1	2	3	4	5	6	7	8
11.	m-Nitroaniline	Brown	5	5	4	4	4
12.	p-Nitroaniline	Brown	5	5	4	4	4
13.	p-Bromoaniline	Light violet	5	5	4	4	4
14.	p-Fluoroaniline	Brown	5	5	4	3-4	3-4
15.	p-Phenitidine	Brown	5	5	4	4	4
16.	5-Cl-2-Me-Aniline	Brown	5	5	4	4	4
17.	5-Nitro-2-Me-Aniline	Brown	5	5	4	3-4	4
18.	5-Nitro-o-Anisidine	Gray	5	5	4	4	4
19.	a-Naphthyl amine	Brown	5	5	4	4	4
20.	B-Naphthyl amine	Violet	5	5	4	4	3-4

TABLE 5

Reactive Azoic Dyeing of Wool with Reactive Anthracenol Base, Colour, Fastness Properties.

No.	Base	Colour	Washing Fastness		Light Fastness	Rubbing Fastness	
			Staining	Compare to Pattern		Wet	Dry
1	2	3	4	5	6	7	8
1.	Aniline	Red	5	5	7	4	4
2.	o-Toluidine	Red	5	5	5-6	4	4
3.	m-Toluidine	Red	5	5	5-6	4	4
4.	p-Toluidine	Red	5	5	5-6	4	4
5.	o-Anisidine	Red	5	5	6	5	4-5
6.	p-Anisidine	Scarlet	5	5	6-7	4-5	4-5
7.	o-Cl-aniline	Scarlet	5	5	6-7	4	4
8.	m-Cl-aniline	Red	5	5	6	4	4
9.	p-Cl-aniline	Scarlet	5	5	5-6	4-5	4
10	o-Nitro-aniline	Red	5	5	5-6	4-5	4-5

TABLE 5 contd.

1	2	3	4	5	6	7	8
11.	m-Nitro-aniline	Orange	5	5	6	4-5	4-5
12.	p-Nitro-aniline	Scarlet	5	5	6-7	4-5	4-5
13.	p-Bromo-aniline	Scarlet	5	5	7	4-5	4-5
14.	p-Fluoro-aniline	Scarlet	5	5	5-6	4	4
15.	p-Phenitidine	Scarlet	5	5	6	4	4
16.	5-Cl-2-Me-aniline	Scarlet	5	5	6	4-5	4-5
17.	5-Nitro-2-Me-aniline	Scarlet	5	5	7	4-5	4-5
18.	5-Nitro-o-anisidine	Brown	5	5	7	5	5
19.	a-Naphthylamine	Brown	5	5	6-7	4-5	5
20.	B-Naphthylamine	Brown	5	5	6-7	4-5	5

TABLE 6

Reactive Azoic Dyeing of Wool with Reactive Anthracenol Base, Colour and Fastness Properties.

No.	Base	Colour	Washing Fastness		Light Fastness	Rubbing Fastness	
			Staining	Compare to pattern		Wet	Dry
1	2	3	4	5	6	7	8
1.	Aniline	Brown	5	5	6	4	4
2.	o-Toluidine	Brown	5	5	5-6	4	4
3.	m-Toluidine	Brown	5	5	5-6	4	4
4.	p-Toluidine	Brown	5	5	5	4-5	4
5.	o-Anisidine	Brown	5	5	5	5	4
6.	p-Anisidine	Brown	5	5	6	4	4-5
7.	o-Chloroaniline	Reddish brown	5	5	6	4	4
8.	m-Chloroaniline	Brown	5	5	5	4-5	4
9.	p-Chloroaniline	Brown	5	5	4-5	5	4
10.	o-Nitroaniline	Reddish Brown	5	5	5	4-5	4-5

TABLE 6 (contd.)

1	2	3	4	5	6	7	8
11.	m-Nitroaniline	Brown	5	5	5	4	5
12.	p-Nitroaniline	Brown	5	5	6	4-5	4-5
13.	p-Bromoaniline	Light violet	5	5	6	5	4
14.	p-Fluoroaniline	Brown	5	5	5	4	5
15.	p-Phenitidine	Dark brown	5	5	5	4	4
16.	5-Cl-2-Me-Aniline	Brown	5	5	5	4-5	4
17.	5-Nitro-2-Me-Aniline	Brown	5	5	6	4-5	5
18.	5-Nitro-o-Anisidine	Gray	5	5	6	5	5
19.	a-Naphthyl amine	Dark brown	5	5	6	4-5	4-5
20.	B-Naphthyl amine	Dark brown	5	5	6	4-5	4-5

cotton and red to scarlet shades on wool fibres. The reactive anthracenol produces brown shades on cotton and wool fibres. The shades obtained on the fibres are bright in colour and are uniform (Appendix I).

It is a well known fact that increase in molecular weight of naphthols in azoic dyeing by increasing the complexity of the fused ring systems in naphthols leads to greater substantivity and also has a bathochromic effect. Comparison of shades of reactive anthracenol with that of reactive naphthol showsthat reactive anthracenol gives higher shades than that of reactive naphthol.

The comparision of the shades on cotton and wool proves that wool shows higher substantivity to the reactive components than cotton.

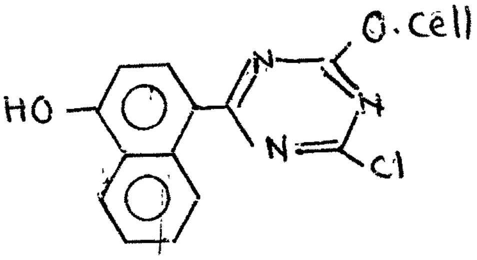
3.4.2 Nature of Reactive Azoic Dyes

Generally azoic dyes are soluble in cold chloroform and give a coloured solution when the pattern is shaken with this solvent in a test tube. In the present investigation, no coloured solution was observed when the dyed hanks were shaken with cold chloroform solution. The behaviour of the dyed fibres in 20% boiling pyridine solution was also observed. No colour change was noticed when the fibres were boiled with 20% pyridine solution in a test tube.

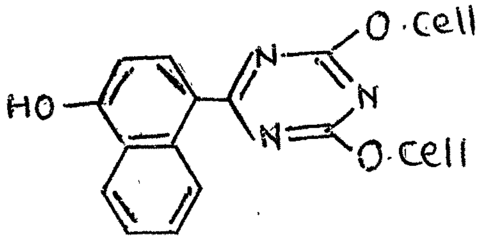
Bode has suggested a method for distinguishing reactive dyeings from that of azoic dyeing (35). Azoic dyes can be removed by extracting with pure dimethylformamide and/or a mixture of ethanol and glacial acetic acid. Here azoically dyed fibres with reactive naphthol and reactive anthracenol did not show any change on treating them with dimethylformamide and/or a mixture of ethanol and glacial acetic acid. Thus fibres dyed with reactive naphthol and reactive anthracenol in azoic dyeing show more characteristics of reactive dyeing than azoic dyeing. This must be due to the covalent bond formation between reactive coupling components and fibres

For studying the crosslinking behaviour of reactive dye with the cellulose fibre, insolubility in a suitable solvent is observed (36-38). Mack et al have used electron microscope to prove the formation of a cross-linked structure (39). Recently Betrabet, Baqwe and Daruwalla have reported different analytical techniques viz. electron microscopy, surface area determination and swelling in cadoxen solvent for obtaining positive evidence for the formation of cross-links between adjacent cellulose chains in cotton dyed with bifunctional reactive dyes (40). In the present study the method suggested by Vickerstaff was used (41). The dyed hank was reduced with alkaline sodium hydrosulphite and the amine produced on the fibre was diazotized using 10% cold hydrochloric acid and sodium nitrite and then coupled with alkaline solution of B-naphthol. A green-orange shade on the fibre was obtained. The wet fastness property of this fibre was found the same as that of the original fibre, thus giving the clue of covalent bond formation between reactive component and the fibre.

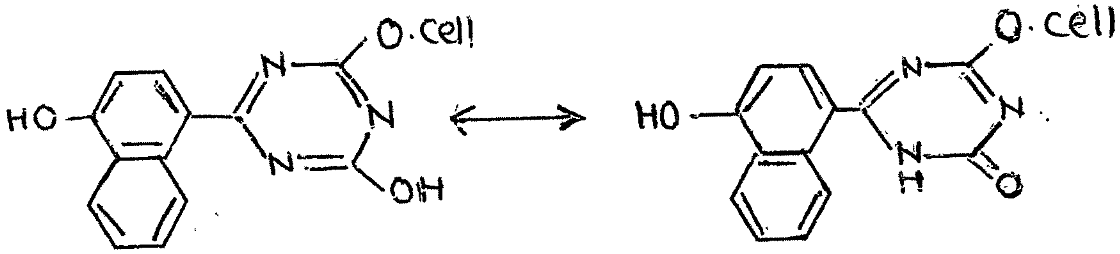
Dawson, Fern and Preston have suggested that three types of dyeing are possible when cellulose is dyed with reactive dyes (37,42). Considering that the behaviour or reactive dye and reactive naphthol should be same, then, following three types of linkages between reactive naphthol and cellulose are possible



Type-1



Type-2



Type-3

Type I possibility was eliminated by the fact that no reactive chlorine was found to be present on the fibre. The detection of reactive chlorine on the fibre was performed by pyridine caustic soda reaction (42).

To check whether type 3 dyeing has taken place or not, the compound 2-chloro-4-hydroxy-6-(4'-hydroxy-1'-naphthyl)-s-triazine was prepared. It was prepared by hydrolysing the compound 2,4-dichloro-6-(4'-hydroxy-1'-naphthyl)-s-triazine at room temperature with aqueous sodium hydroxide. The unhydrolysed dichloro compound was repeatedly extracted with boiling toluene. The red colour residue has melting point $> 300^{\circ}C$ and was analysed for C, H and N. (For $C_{13}H_8N_3ClO_2$ require % C 57.03; % H 2.925 and % N 15.36 ; found % C 57.42; % H 2.737 and % N 14.96). This compound was used as reactive naphthol in azoic dyeing. Dyeing was performed at 70 to 80°C, keeping all other conditions the same as previously mentioned. When the fibre was developed with diazotised aniline, red colour was obtained. The higher shade obtained suggests that type 3 dyeing is not possible, as the previous naphthol gives pink colour.

The change of colour obtained can be explained by comparing the absorption spectra of both the naphthols (Fig 3). The spectra were taken on a spekol spectrophotometer with 10 mm cell using acetone as solvent. The naphthol having two chlorine atoms shows a strong absorption at 450 nm, while the other with a chlorine and a hydroxyl group in s-triazine ring shows two absorption peaks at 450 nm(inflection) and at 530 nm. In the later case, two absorptions can be attributed due to keto-enol tautomerism. In

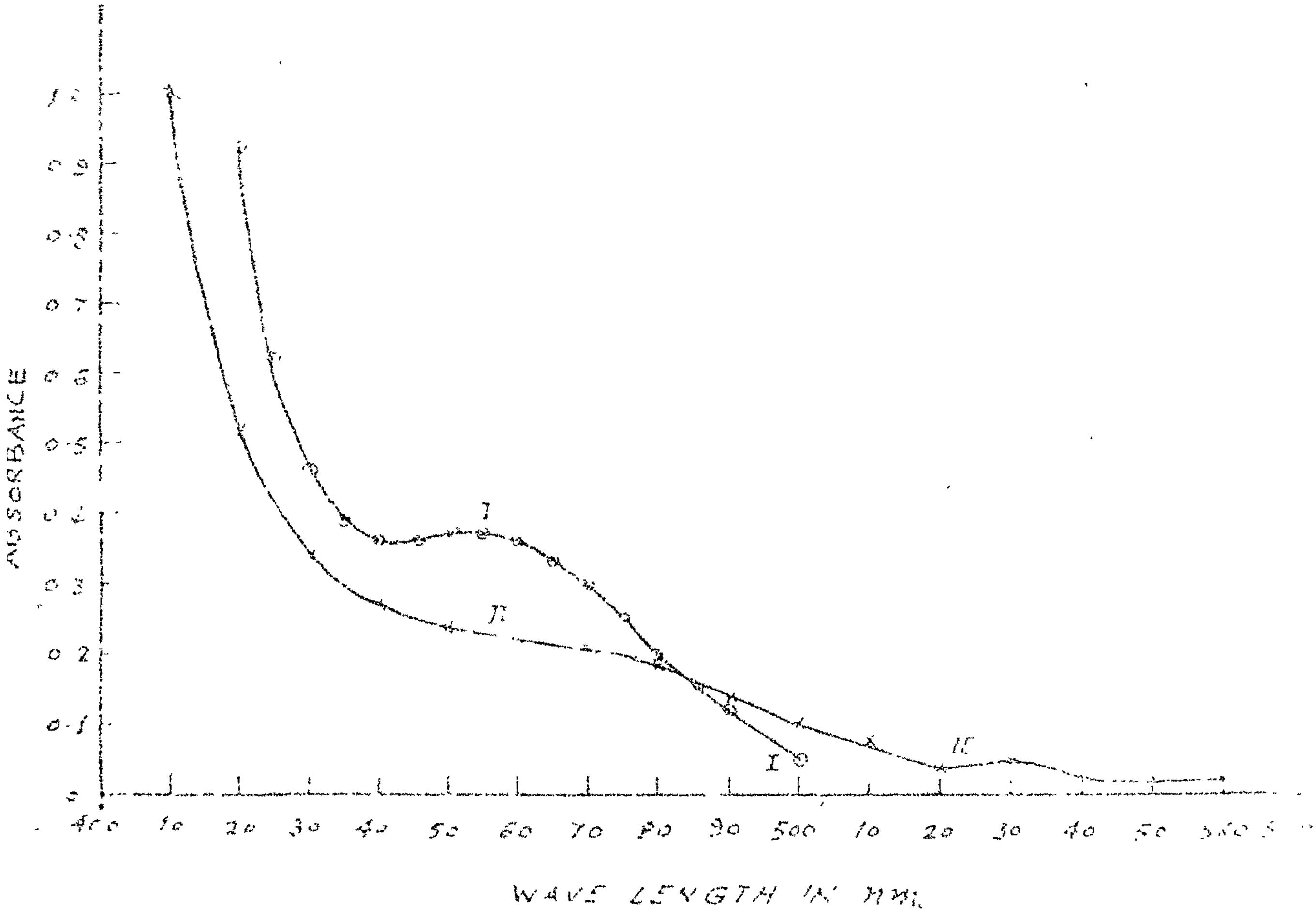


Fig. 3 Absorption spectra of (I) 2,4-dichloro-6(4'-hydroxy-1'-naphthyl)-s-triazine and (II) 2-chloro-4-hydroxy-6-(4'-hydroxy-1'-naphthyl)-s-triazine in acetone.

these types of compounds, such tautomerism has been suggested by Wegmann in view of abnormally low reactivity of such compounds (43).

After eliminating the two possibilities of bonding type 1 and type 3, type 2 is only possible. Type 2 was further confirmed by the solubility behaviour of dyed fibres in conc sulphuric acid (36). The dyed fibre was found insoluble in 50% sulphuric acid but was soluble in 80% sulphuric acid. Parallel solubility behaviour was shown when the fibre was treated with cupraammonium hydroxide solution. The fibre remained insoluble suggesting the presence of type 2 bonding (44,45).

3.4.3 Fastness Properties

Colour fastness of textile is the resistance of a dyeing to different agencies to which it may be exposed during manufacture and subsequent use. It is well known that the same dye may exhibit considerable differences in fastness properties according to the nature of the fibre which is dyed, the weave and surface characteristics of the fibre, the depth of the shade and other factors. For fastness determination various standard organisation like ISO, SDC, AATCC, ICI describe the test methods in great detail. Degree of colour change is adopted as standard for classifying the effect of different agencies on a dyeing. In the present study gray scale for assessing colour changes is used.

For washing and rubbing fastness following scale is used:

Class	Grade
5	excellent
4	good
3	fair
2	poor
1	very poor

While for light fastness following terms are used.

8	outstanding
7	excellent
6	very good
5	good
4	fairly good
3	fair
2	poor
1	very poor

3.4.3.1 Washing Fastness

The washing fastness is an important consideration for azoic dyes on cotton. The action of boiling caustic soda solution or azoic colour has been extensively studied by Rowe et al. (46-49). Several workers have tried to generalise the relation between structure of naphthol and washing fastness (50-52). But in case of reactive azoic dyes no structural effect is observed on washing fastness. The washing fastness of all dyed materials is found of the highest grade. The reason is obvious-covalent bond formation between reactive naphthol (also reactive anthracenol) and fibre.

The washing fastness of cotton dyed with reactive naphthol is 5 (staining) and 4-5 (compare to pattern), while for wool it is 5 in both the cases. The fibres, cotton as well as wool, dyed with reactive anthracenol show the washing fastness 5. Thus increase in fused ring system of reactive naphthol increases the washing fastness of cotton fibres (compare to pattern) from 4-5 to 5.

3:4:3:2 Light Fastness

Fastness to light is one of the most important properties a dyed fibre needs in order to fulfil its function over a period of time. The effects of solar radiation falling on a dyed textile are manifested in two principal ways:

(a) a change in the shade and/or depth of shade of the colouration, and

(b) the phydical degradation of the substrate fibre as evidenced by changes in tensile strength, abrasion resistance, etc.

However, the changes in the dye component usually occur in a much shorter time. Therefore, the problems of dye fading is of greater significance than fibre degradation in textiles exposed to sunlight. The effect of light on dyes, both in solution and on textiles and other substrates, has been extensively studied (53-59).

The light fastness of azoic cotton dyeings, which varies over the range 1-2 to 7-8, depends on the nature of both the diazo and coupling components (60). In case of reactive naphthol light fastness are in the range of 4-7 for cotton and 5-7 for wool, while in case of reactive anthracenol light fastness is varied from 4 to 5 for cotton fibres and 5 to 6 for wool fibres. The results indicate that wool fibres are showing more light fastness than cotton fibres. When the two reactive systems are compared for the light fastness property, a little lowering is observed in the reactive anthracenol case. The lowering in light fastness can be explained by considering the easily oxidizable and fluorescent property of azo derivative of 1-anthracenol (61).

3:4:3:3 Rubbing Fastness

The nature of the azoic dyeing process indicates that the main problem in this dyeing is the superficially precipitated pigment, the effect of which is lack of fastness to rubbing. Careful control of the condition of naphtholation, development and after treatment is necessary for producing shades of good fastness to rubbing (62). The rubbing fastness of azoic dyed materials depends upon the substantivity of the naphthol towards fibre and the efficiency of the removal of the azoic pigment by soaping after treatment. These difficulties do not arise in reactive azoic dyeing. For this reason, reactive naphthol shows rubbing fastness of fair to good quality for cotton and good to excellent grade for wool fibres. The rubbing fastness for reactive anthracenol is in the range of 3 to 4 for cotton and 4 to 5 for wool fibres. An increase in rubbing fastness is observed with the increase in the complexity of fused ring systems.

3.4.4 Visible Spectra of Dyed Fibres

The reactive anthracenol gives yellowish green fluorescence in acetone, benzene, dioxane etc. This property induces an error into absorption spectra obtained from a spectrophotometer with an integrating sphere because most of the fluorescent radiation is added to the transmitted energy, thus increasing the apparent transmittance. Problems in measuring fluorescence (63), combined with the many factors that influence it in solution as well as on the subtrate (64,65) lesser the probability of good correlation between reactive naphthol and reactive anthrecenol. Therefore, to study the effect of increased fused ring system of reactive coupling components and effect of different substituents in diazo component on the visible spectrum of dyed fibres, dissolution method for dyed fibres was used. The sulphuric acid method is probably the oldest of all dissolution methods for the determination of dyes in fibres (66). Waters determined the dye spectrophotometrically after dissolving the dyed fabric in cold 80% sulphuric acid (67). Yakarina and Lapkina used concentrated sulphuric acid to dissolve viscose rayon mass-coloured with pigments (68). In the present investigation the method suggested for cotton by Kissa for reactive dyes was used (69).

20 mg of dyed cotton was dissolved in 2.5 ml conc sulphuric acid at 5 to 10°C. After an hr, the solution was diluted with 20 ml of cold distilled water. The solution was allowed to stand at room temperature for 10 min. Brown has suggested the use of aminoethylcellulose flock at this stage, to absorb the dye rapidly and then treatment with ammonia, ammonium sulphate, dimethyl formamide etc. (70). In our study, it was found possible to eliminate this procedure safely by extracting the dye from the solution using ethanol free chloroform. The dye was extracted from solution into chloroform and making the volume of chloroform extract to 25 ml. A solution of the same amount of undyed cotton was used as the reference solution for absorbance measurement. The data are given in Table 7 and shown in figs 4 and 5.

TABLE 7

Absorption Spectra of Dyed Fibres

No.	Base	Reactive Naphthol		Reactive Anthracenol	
		Cotton (chloroform)	Wool (n-butanol)	Cotton (chloroform)	Wool (n-butanol)
1	2	3	4	5	6
1.	Aniline	515	500	530 inf.	530 inf.
2.	o-Toluidine	510	500	540 inf.	525 inf.
3.	m-Toluidine	510	515	525	520
4.	p-Toluidine	520	505	535	525
5.	o-Anisidine	520	510	540	530
6.	p-Anisidine	480 inf.	515	500	525
7.	o-Cl-Aniline	505	500 inf.	530	540 inf.
8.	m-Cl-Aniline	480	490 inf.	520	495
9.	p-Cl-Aniline	490 inf.	500	520 inf.	505
10.	o-Nitroaniline	510	490	520 inf.	530 inf.

TABLE 7 (contd)

1	2	3	4	5	6
11	m-Nitroaniline	485	490 inf.	515 inf.	530 inf.
12	p-Nitroaniline	480	470 inf.	510 inf.	505
13	p-Bromoaniline	510	500	525	515
14	p-Fluoroaniline	470 inf.	485	515 inf.	500
15	p-Phenitidine	520	520	530	530
16	5-Cl-2-Methylaniline	510 inf.	500	530	520
17	5-Nitro-2-Methylaniline	500	500	520 inf.	520
18	5-Nitro-o-Anisidine	525	510	530 inf.	500
19	a-Naphthylamine	510 inf.	515	515	520 inf.
20	B-Naphthylamine	515	520	535	550

inf = inflection

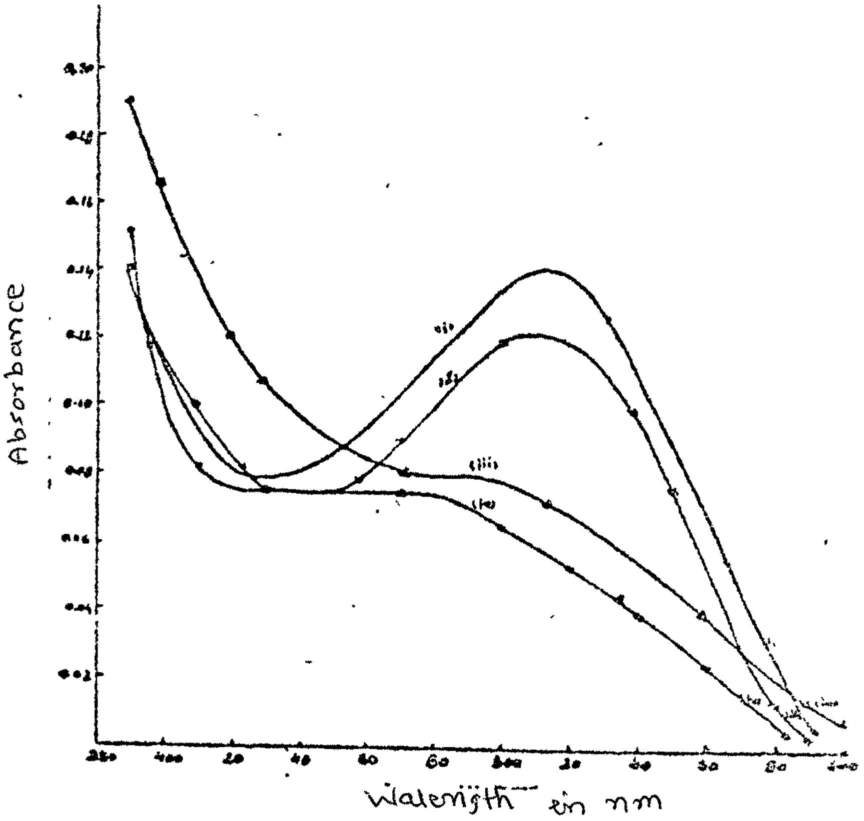


Fig.4 Visible spectra of cotton fibres dyed with reactive naphthol and base (i) Aniline, (ii) o-Toluidine, (iii) p-Chloro aniline and (iv) p-Anisidine.

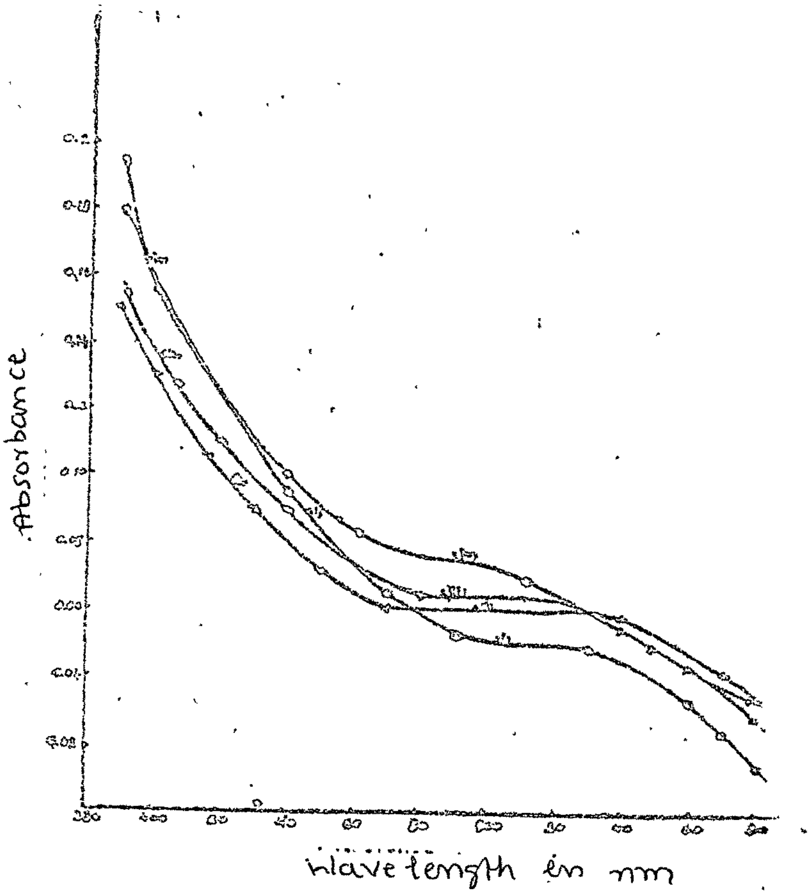


Fig.5 Visible spectra of cotton fibres dyed with reactive anthracenol and base (i) Aniline, (ii) o-Toluidine, (iii) p-chloro aniline and (iv) p-Anisidine.

Wool is soluble in sodium hydroxide, alkaline solutions of sodium hypochlorite, cadoxen (71), and zincoxen (72). Giles and Shaw heated dyed wool with boiling 10% sodium hydroxide for 2 min and extracted the turbid alkaline solution with pyridine to get a clear solution for spectrophotometric dye determination (73). Odvarka et al. used a similar method for determining disperse dyes in wool, but used ethyl acetate to extract the dye from alkaline (5% NaOH) solution (74). Delmenico and Peters dissolved wool dyed with acid dyes (10-40 mg) in 3 N (1 ml/10 mg) wool) sodium hydroxide at room temperature (20 hrs) . The solution was diluted with o-chlorophenol to 25 ml, and diluted further, if necessary with o-chlorophenol containing 1 ml 3 N sodium hydroxide per 50 ml (75). It was found advantageous to use n-butanol as solvent for extracting dye from wool dissolved in aqueous sodium hydroxide and acidified the solution with dil hydrochloric acid. The dye solutions were stable for several days. The results are given in Table 7 and some are shown in figs 6 and 7.

Generally the broad peaks are obtained while in few cases only an inflection is observed. The visible spectra of the dyes in chloroform is generally having a

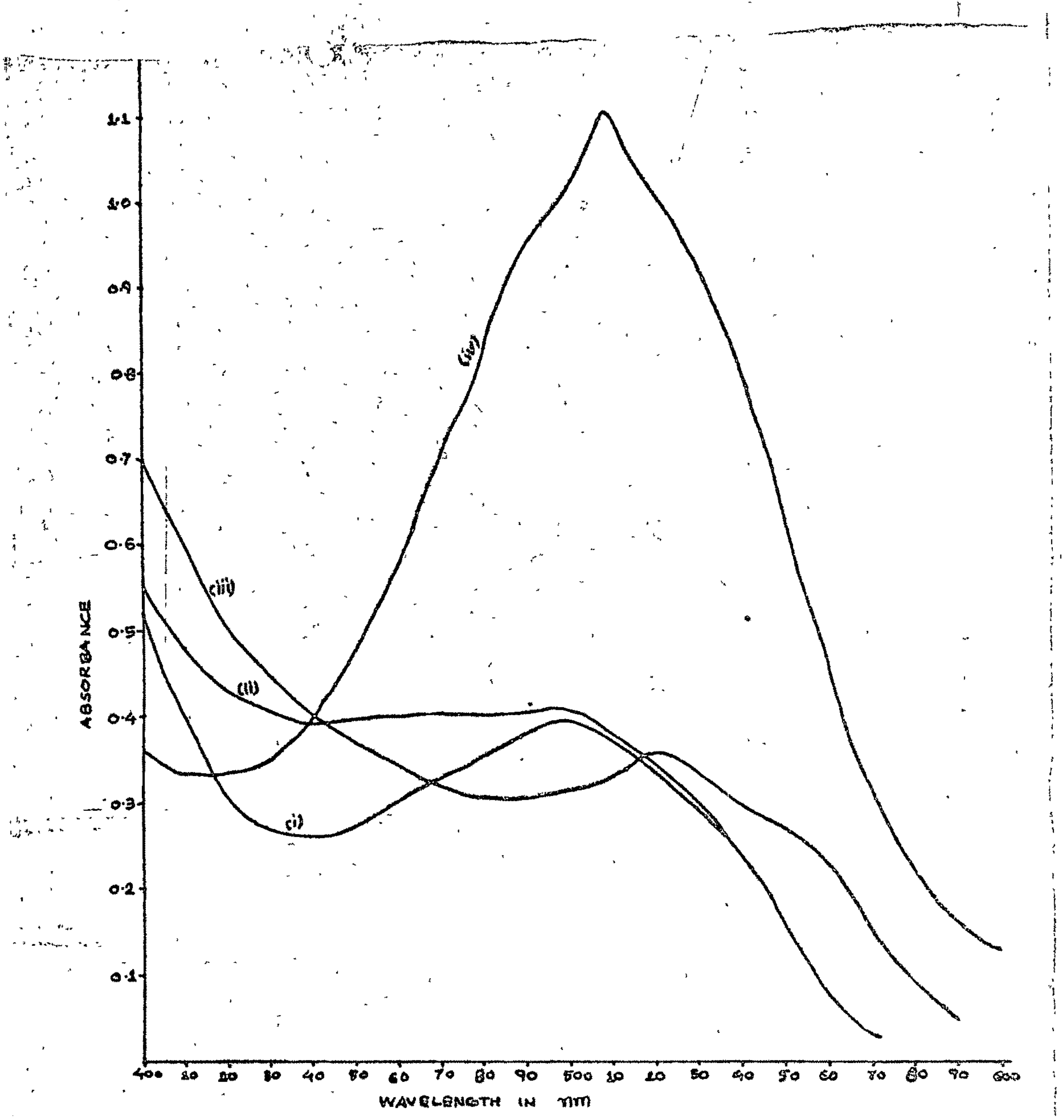


Fig.6 Visible spectra of wool fibres dyed with reactive naphthol and base (i) Aniline, (ii) p-Fluoro aniline, (iii) β-Naphthyl amine and (iv) 5-Nitro-o-anisidine.

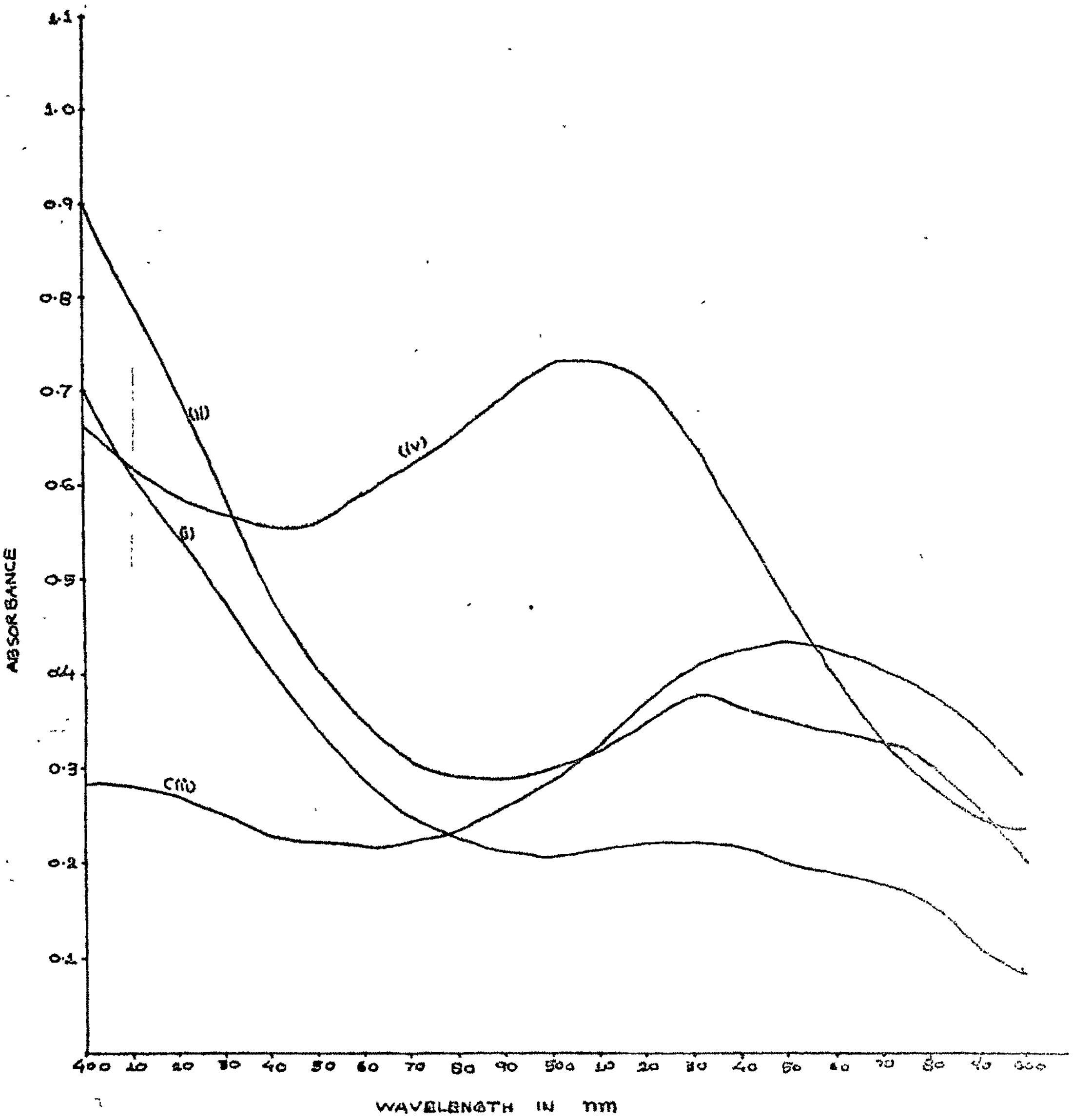


Fig.7 Visible spectra of wool fibres dyed with reactive anthracenol and base (i) p-Anisidine, (ii) P-Phenitidine, (iii) β-Naphthyl amine and (iv) P-Chloro aniline.

red shift as compared to the spectra in n-butanol, with a few exceptions. Similarly the fibres dyed with reactive anthracenol have a greater λ max as compared to reactive naphthol in both the solvents. This is due to the increase in conjugation e.g. the benzene ring. As the naphthalene and anthracene have the spectra in UV region (76)

		λ max	
Naphthalene	221	289	315
Anthracene	255	379	-

The effect of substitution in the naphthalene and anthracene ring perturb the structure of the molecule. Generally the nitro substituted dyes have the lower shift in λ max as compared to other substituent viz. halogen, methoxy etc. The lower shift of nitro group is may be due to the resonance structure as observed in the nitro-benzene (17). The same observations are recorded with the halogen substituted dyes since it is believed that the halogens have a mesomeric effect arising from resonance benzenoid and quinonoid forms which give the lower shift. The methoxy group is an electro negative substituent (77), the possible tautomeric effect is much more powerful than the inductive effect and causes a further red shift (78).

3.4.5 Halo Aromatic Amines in Reactive Azoic Dyeing of Cotton and Wool

Brocker et al. in their study on reactive naphthols have taken several reactive coupling components and developed the cotton fibres with o-chloro-and m-chloro-anilines (34). It was thought to study systematically the effect of halo aromatic amines in reactive azoic dyeing of cotton and wool. Both the reactive coupling components, reactive naphthol and reactive anthracenol were impregnated on cotton and wool. The fibres were developed with fifteen diazotized halo aromatic amines. All halo aromatic amines used were of Koch Light Laboratories, England. The shades obtained and the fastness properties are given in Tables 8 to 11.

All halo aromatic amines produce attractive shades on cotton as well as on wool, varied from orange to violet. Dyeings with reactive anthracenol imparts dull hues in comparision with reactive naphthol on both the fibres, irrespective of halo aromatic amines used. This indicates that effect of hue of the fibres depends more on the nature of reactive coupling components than the amines used for developing purpose.

TABLE 8

Reactive Azoic Dyeing of Cotton with Reactive Naphthol

Halo Aromatic Amines, Colour and Fastness Properties

No.	Halo Aromatic Amine	Colour	Washing Fastness		Light Fast -ness	Rubbing Fastness	
			Staining	Compare to Pattern		Wet	Dry
1	2	3	4	5	6	7	8
1	p-Fluoro aniline	Orange	5	4-5	4	3-4	3-4
2	p-Chloro aniline	Orange	5	4-5	4-5	4	4
3	p-Bromo aniline	Red	5	5	5	4	4
4	p-Iodo aniline	Red	5	5	5-6	4	4
5	o-Fluoro aniline	Orange	5	4-5	4	3-4	3-4
6	o-Chloro aniline	Scarlet	5	5	4-5	3	3-4
7	m-Fluoro aniline	Orange	5	4-5	4	3-4	3

TABLE 8 (contd)

1	2	3	4	5	6	7	8
8	m-Chloro aniline	Orange	5	4-5	4	3	3-4
9	2,3-Dichloro aniline	Orange	5	5	5	4	4
10	2,4-Dichloro aniline	Orange	5	5	5-6	4	4-5
11	2,6-Dichloro aniline	Orange	5	5	5-6	4	4-5
12	3,4-Dichloro aniline	Orange	5	5	5	4	4
13	o-Amino benzotrifluoride	Reddish-Orange	5	5	5-6	4-5	4-5
14	m-Amino benzotrifluoride	Reddish-Orange	5	5	5	4	4-5
15	p-Amino benzotrifluoride	Reddish-Orange	5	5	5-6	4	4-5

TABLE 9

Reactive Azoic Dyeing of Cotton with Reactive Anthracenol

Halo Aromatic Amines, Colour and Fastness Properties

No	Halo Aromatic Amine	Colour	Washing Fastness		Light Fast-ness	Rubbing Fastness	
			Staining	Compare to pattern		Wet	Dry
1	2	3	4	5	6	7	8
1	p-Fluoro aniline	Brown	5	5	4	3-4	3-4
2	p-Chloro aniline	Brown	5	5	4	3-4	4
3	p-Bromo aniline	Light violet	5	5	4	4	4
4	p-Iodo aniline	Light violet	5	5	5	4	4
5	o-Fluoro aniline	Scarlet	5	5	4	3-4	3-4
6	o-Chloro aniline	Scarlet	5	5	4	3-4	3-4
7	m-Fluoro aniline	Scarlet	5	5	4	3	3

TABLE 9 contd.

1	2	3	4	5	6	7	8
8	m-Chloro aniline	Scarlet	5	5	4	3	3
9	2,3-Dichloro aniline	Scarlet	5	5	4-5	4	4
10	2,4-Dichloro aniline	Scarlet	5	5	5	4	4-5
11	2,6-Dichloro aniline	Scarlet	5	5	4-5	4-5	4-5
12	3,4-Dichloro aniline	Scarlet	5	5	4-5	4	4-5
13	o-Amino benzotrifluoride	Scarlet	5	5	4-5	4-5	4
14	m-Amino benzotrifluoride	Scarlet	5	5	4	4	4
15	p-Amino benzotrifluoride	Scarlet	5	5	4-5	5	4-5

TABLE 10

Reactive Azoic Dyeing of Wool with Reactive Naphthol

Halo Aromatic Amines, Colour and Fastness Properties

No.	Halo Aromatic Amines	Colour	Washing Fastness		Light Fastness	Rubbing Fastness	
			Staining	Compare to pattern		Wet	Dry
1	2	3	4	5	6	7	8
1	p-Fluoro aniline	Scarlet	5	5	5-6	4	4
2	p-Chloro aniline	Scarlet	5	5	5-6	4-5	4
3	p-Bromo aniline	Scarlet	5	5	7	4-5	4-5
4	p-Iodo aniline	Dark Red	5	5	7	5	5
5	o-Fluoro aniline	Scarlet	5	5	6	4	4
6	o-Chloro aniline	Scarlet	5	5	6-7	4	4
7	m-Fluoro aniline	Red	5	5	5	4	4

TABLE 10 contd.

1	2	3	4	5	6	7	8
8	m-Chloro aniline	Red	5	5	6	4	4
9	2,3-Dichloro aniline	Red	5	5	6-7	4-5	4-5
10	2,4-Dichloro aniline	Red	5	5	7	5	5
11	2,6-Dichloro aniline	Red	5	5	6-7	5	5
12	3,4-Dichloro aniline	Red	5	5	6	4-5	5
13	o-Amino benzotrifluoride	Dark Red	5	5	6-7	5	5
14	m-Amino benzotrifluoride	Dark Red	5	5	6-7	5	5
15	p-Amino benzotrifluoride	Dark Red	5	5	6-7	5	5

TABLE 11

Reactive Azoic Dyeing of Wool with Reactive Anthracenol

Halo Aromatic Amines, Colour and Fastness Properties

No.	Halo Aromatic Amine	Colour	Washing Fastness		Light Fastness	Rubbing Fastness	
			Staining	Compare to pattern		Wet	Dry
1	2	3	4	5	6	7	8
1	p-Fluoro aniline	Brown	5	5	5	4	5
2	p-Chloro aniline	Brown	5	5	4–5	5	4
3	p-Bromo aniline	Brown	5	5	6	5	4
4	p-Iodo aniline	Brown	5	5	6	5	4
5	o-Fluoro aniline	Reddish brown	5	5	6	5	4
6	o-Chloro aniline	Reddish brown	5	5	6	5	4
7	m-Fluoro aniline	Brown	5	5	5	4	4

TABLE 11 contd.

1	2	3	4	5	6	7	8
8	m-Chloro aniline	Brown	5	5	5	4-5	4
9	2,3-Dichloro aniline	Brown	5	5	6	5	4-5
10	2,4-Dichloro aniline	Reddish Brown	5	5	6	5	5
11	2,6-Dichloro aniline	Light Brown	5	5	6	5	5
12	3,4-Dichloro aniline	Light Brown	5	5	5	5	5
13	o-Amino benzotrifluoride	Brown	5	5	6	5	5
14	m-Amino benzotrifluoride	Brown	5	5	5-6	5	5
15	p-Amino benzotrifluoride	Brown	5	5	6	5	5

The effect of fluorine compounds as bases in azoic dyeing is to improve the clarity of the tone and light fastness but to reduce washing fastness (79). In our observation we have noted that whichever the base is used, whether containing halogen or not, clear tone on the dyed fibre is obtained. Some marginal change in light fastness due to halogen substituent is noted and no change in washing fastness is taking place. This must be due to the fact that in reactive azoic dyes, washing fastness is governed by the extent of covalent bonding of naphthol to the fibre. The reactive naphthol and reactive anthracenol form covalent bond with the fibre.

To understand the behaviour of halo aromatic amines, unsubstituted amine aniline was taken for developing purpose. The shade obtained and fastness properties are given in Table 12. From the comparision of washing fastness it is revealed that introduction of halogen in the diazo component do not change the washing fastness. washing fastness of the fibres are in the range of 4 to 5.

It is a well known fact that in azoic dyeing, those substituents on the aniline component that withdraw

TABLE 12

Colour and Fastness Properties for Aniline

No.	Properties	Reactive Naphthol		Reactive Anthracenol	
		Cotton	Wool	Cotton	Wool
1.	Colour	Pink	Red	Light bourdex	Brown
2	λmax in nm	515	500	530 inf.	530 inf.
3	Washing Fastness				
	Staining	5	5	5	5
	Compare to Pattern	4-5	5	5	5
4	Light Fastness	6	7	5	6
5	Rubbing Fastness				
	Wet	3-4	4	4	4
	Dry	4	4	4	4

inf = inflection

electrons from the azo group, notabley trifluoromethyl and nitro groups, increase the light fastness, on the other hand, electron donating substituents, such as methyl and methoxy groups ortho to the azo group, decrease the light fastness. Fluorine containing substituents in the diazo component have been reported to increase significantly the light fastness of azoic dyes (80). It is seen from the data of light fastness that introduction of low molecular weight halogen i.e. F - and Cl - in the benzene ring at -o, -m or -p positions lower the light fastness. In case of p-bromo and p-iodo anilines, nearly same light fastness with aniline is observed, but in none of the cases the introduction of halogen has increased the light fastness. The dichloro derivatives and benzotrifluoride derivatives are also not improving the light fastness of both the fibres cotton and wool for both reactive components.

Rubbing fastness remains unaltered due to introduction of halogen. However, wool fibres show some increase in rubbing fastness.

The effect of increased fused ring system i.e. from reactive naphthol to reactive anthracenol on shade of the fibres and fastness properties remains same irrespective of amine used.

The visible spectra of dyed fibres are shown in Table - 13. Generally the spectra of benzene affected markebly by substitution. A substitution is supposed to purturb the benzene ring both by resonance and inductive effects (81,82). A substitution with positive inductive effects lower the ionisation energy of the substituted benzene, while one with the negative effect increases it. The resonance effect lowers the ionisation energy of the molecules. The variation of the ionisation energy is seen in terms of wavelength shift. The polar groups containing the unshared electrons (NH_2) shifts the absorption bands to longer wavelengths. Bowden and Braude have studied the spectra of a number of benzene derivatives containing the groups F, Cl, Br, and I and found that the spectra bears no simple relation (83). The visible spectra of azo dyes derived from halo aromatic amines show a close resemblence with substituted benzenes. In the para position of the azo compounds the inductive (I) effect should be smaller as compared to meta and ortho positions because of increased distance. A group has a

TABLE 13

Absorption Spectra of Dyed Fibres

No.	Base	Reactive Naphthol		Reactive Anthracenol	
		Cotton (Chloroform)	Wool (n-butanol)	Cotton (Chloroform)	Wool (n-butanol)
1	2	3	4	5	6
1	p-Fluoro aniline	470 inf.	485	515	500
2	p-Chloroaniline	490 inf.	500	520	505
3	p-Bromo aniline	510	500	525	515
4	p-Iodo aniline	510	500	520	520
5	o-Fluoro aniline	505	500	520 inf.	520
6	o-Chloro aniline	505	500	530	540
7	m-Fluoro aniline	470	490	510	490

TABLE 13 contd.

1	2	3	4	5	6
8.	m-Chloro aniline	480	490	520	495
9.	2,3-Dichloro aniline	495	500	525	520
10.	2,4-Dichloro aniline	505	515	530	520
11	2,6-Dichloro aniline	480	480	515	515
12	3,4-Dichloro aniline	500	510	510	520
13	o-Amino benzotrifluoride	490 inf.	480	500 inf.	500
14	m-Amino benzotrifluoride	495	485	510 inf.	500
15	p-Amino benzotrifluoride	500	495	520	510

inf = inflection

negative inductive and positive tautomeric effect, the electron withdrawing effect is less in p- position as found in halogen substituents and they have the greater shift, the λmax order of azo dyes compounds

$$\mathrm{I} > \mathrm{Br} > \mathrm{Cl} > \mathrm{F}$$

and the order of positions as

$$o- > m- > p-$$

in all the cases is observed except amino benzotrifluoride derivatives where this order is not observed. The same observation in halogen substituted benzene derivatives is reported (84).

3.4.6 Effect of Covalent Bond between Fibre and Reactive Coupling Component on Shade and Fastness Properties

The dyeing of cotton by means of azoic colours differs radically from the processes of dyeing with reactive, direct, basic, sulphur and vat colours, since it is not the dye but an intermediate which is absorbed from solution, and the dye is formed on the fibre by the interaction of two components. The substantivity of the nephthol and mechanically retained on the fibre play prominent role in fastness properties. While in reactive azoic dyeing, chemical bond formation is taking place and fastness properties soley depends on it. It was proposed to study the effect of covalent bond between fibre and reactive coupling component on shade and fastness properties.

1-Anthracenol was used as a coupling component for azoically dyeing cotton and wool. Different amines were used to develop the fibres. The shades obtained and fastness properties are given in Tables 14 and 15. These are compared with the fibres dyed with reactive anthracenol.

3.4.6.1. Effect on Shade

Fibres, cotton and wool, dyed with 1-anthracenol produce reddish borwn to brown shades. Reactive anthracenol also give the shade of same range. No noticeable change in shade is observed. This was further confirmed by comparing the absorption spectra of dyed fibres. Azoic dye was extracted with chloroform and spectra was taken. In fig. 8 spectra of chloroform extract of fibres dyed with 1-anthracenol and reactive anthracenol developed

TABLE 14

1-Hydroxyanthracene* as Coupling Component

Base, Shade on the Cotton Fibre and Fastness Properties

No.	Base	Shade on the Fibre	Washing Fastness	Light Fastness	Rubbing Fastness
1	o-Toluidine	Brown	3	2	2
2	p-Toluidine	Light purple	2	3	2
3	p-Anisidine	Brown	3	2	2
4	o-Nitro aniline	Reddish brown	4	3	2
5	m-Nitro aniline	Brown	4	3	2
6	o-Chloro aniline	Light Scarlet	3-4	3	2
7	m-Chloro aniline	Brown	4	3	2
8	p-Chloro aniline	Brown	3-4	3	2

* Also refered as 1-anthracenol

TABLE 15

1-Hydroxyanthracene* as a Coupling Component

Base, Shade on Wool Fibre and Fastness Properties

No.	Base	Shade on the Fibre	Washing Fastness	Light Fastness	Rubbing Fastness
1	o-Toluidine	Brown	3-4	2-3	2
2	p-Toluidine	Brown	3	3	2
3	p-Anisidine	Brown	3-4	2-3	2
4	o-Nitro aniline	Reddish brown	4	3-4	2
5	m-Nitro aniline	Brown	4	3-4	2
6	o-Chloro aniline	Reddish brown	4	4	2
7	m-Chloro aniline	Brown	3-4	4	2
8	p-Chloro aniline	Brown	4	3-4	2

* Also refered as 1-anthracenol

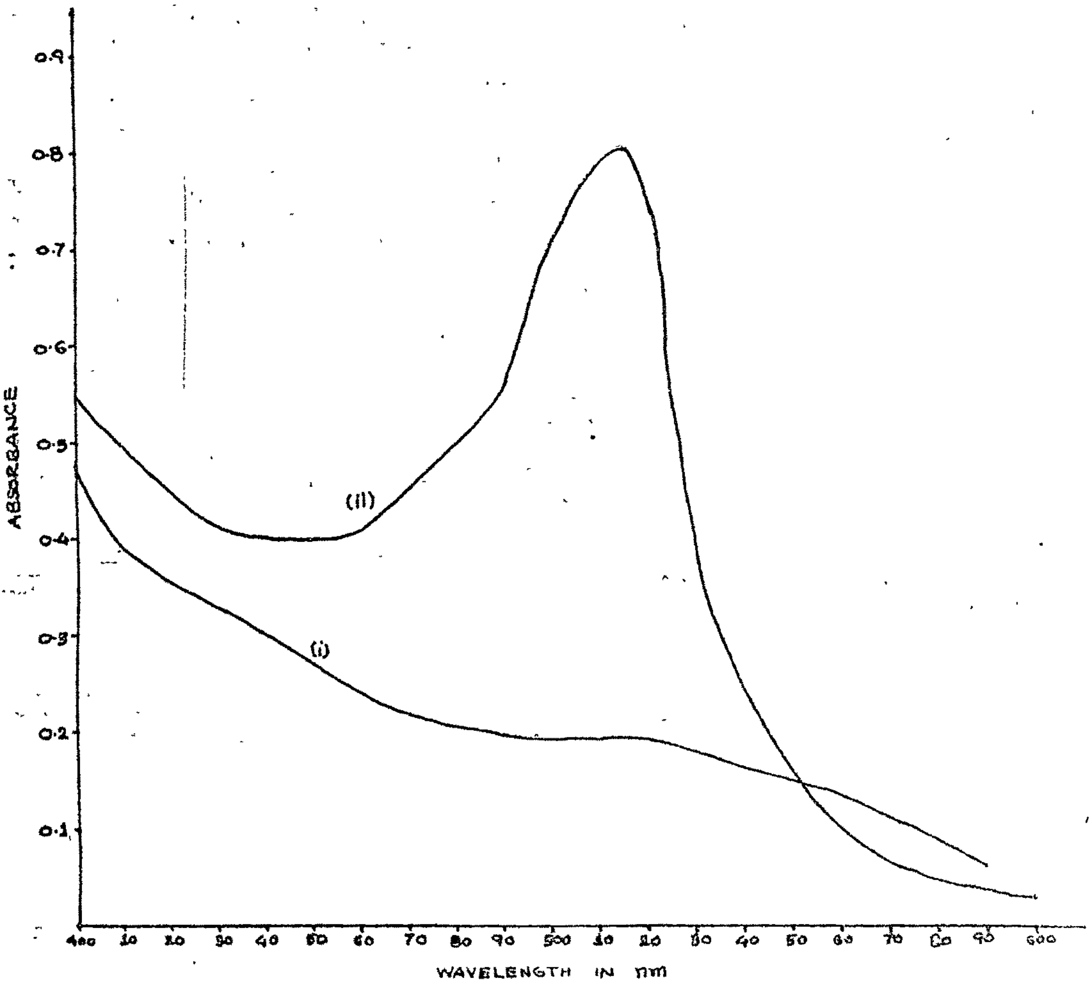


Fig.8 Visible spectra of cotton fibres dyed with (i) reactive anthracenol and (ii) 1-anthracenol. Base used is p-chloro aniline.

with p-chloro aniline are shown. It is seen that 1-anthracenol dye absorbs at 525 while reactive anthracenol gives maxima at 520 nm. Thus only 5 nm red shift is observed when s-triazine ring is introduced into 4-position of 1-anthracenol.

3.4.6.2 Washing Fastness

Washing fastness is reported by compare to pattern method. For cotton fibres it is in the range of 2 to 4, while for wool fibres it is varied between 3 and 4. The reactive anthracenol shows washing fastness of excellent grade for both the fibres. This clearly indicates that capacity of reactive anthracenol to form covalent bond with **fibre** results the increase in washing fastness.

3.4.6.3 Light Fastness

The effect on the light fastness of reactive dyes of the covalent chemical bond to the substrate is the subject of discussion. If a reactive dye is considered as a solubilized chromophere to which is attached a reactive group, then intuitively one would expect the light fastness to be essentially identical to the nonreactive dye constituted from the identical chromophore (this assumes that the reactive group is not electronically integrated with the chromophore). Also it is now known that in addition to the chemical structure of a dye, its physical state in a substrate influences the photo-decomposition during exposure to light. The mode of combination of reactive dyes with cellulosic substrate appears to indicate that they would exist only as single molecules in the fibre and if that was true, these dyes should fade very rapidly.

Giles and co-workers have observed that reactive dyes like other dyes, have a tendency for aggregation in the fibre (85-87). Daruwalla has indicated an evidence of formation of dimers or higher aggregation of the dye molecule (88). He has compared the light fastness of representatives of a range of reactive dyes with their hydrolyzed nonreactive analoga on cotton. The reactive dyes included examples from the Procion, Cibacron, Remazol, Reactone, Levafix, Primazine and Procinyl classes, and in all cases the covalently-bound dye showed a substantially higher lihgt fastness. In case of Procion dyes, Ingamells (89), Chekalin and Romanova (90) also found that these dyes showed higher light fastness in the reacted form than in hydrolysed unreactive form. Ingamells has explained this on the basis of Schaeffer's view on the physical attraction of dyes for fibre substrates and its effect on the fastness to light of the dye; the covalent linkage facilitates the transfer of photochemical energy from the dye to the fibre, thus increasing the resistance of the dye to photochemical attack (91). Yakharova et al. have reported that covalent bond formation improves the light fastness (92). Studies on Remazol dyes on cellophane films have produced similar results (93).

Studies on reactively dyed wool have shown that there is little or no difference in light fastness attributable to dye fibre binding. For example, covalently bound Remazol and Lanasol reactives showed no difference in photostability compared to the hydrolyzed dye (94), and in some cases a decrease was observed. Similar findings apply to wool dyed with reactive polymethine dyes (95). Covalent attachment of Procinyl reactive dyes to nylone has been shown to bring about little or no change in light fastness compared with unbound dyes (96).

Studies by Russian workers on the light fastness of reactive dyes has been reviewed by Krichevkii et al. (97). On the basis of fading rates of monochlorotriazine and vinyl-sulphone dyes in polyamide and cellulose films, the conclusion was drawn that the nature of the dye-substrate bond (covalent or absorption) has little effect on the light fastness. It has been reported by Giles and Co-workers that light fastness results are inconclusive (98). Datyner, Nicholls and Pailthropes findings have shown that it is not possible to generalise any relationship due to dye-fibre covalent bonding (99). Recently Czechoalovakian researchers have reported photochemical decomposition of some triazine reactive dyes (100).

In this connection it was thought of interest to compare the light fastness of fibres dyed with 1-anthracenol (Tables 14 and 15) with that of reactive anthracenol (Table 4 and 6). The former component did not possess reactive system while the later contains dichloro-s-triazinyl as a reactive system. Both the components are applied on the fibres under identical conditions. From the comparison of the data it reveals that 1-anthracenol gives light fastness in 2 to 3 range on cotton while 3 to 4 on wool fibres. The light fastness for reactive anthracenol is varied from 4 to 5 for cotton fibres and 5 to 6 for wool fibres. Thus it is evident that the covalent bonding between cotton as well as wool and a reactive coupling component increasses the light fastness.

3:4:6:4 Rubbing Fastness

Rubbing fastness of 1-anthracenol in dry condition is reported in Table 14 for cotton and Table 15 for wool fibres. The rubbing fastness of both the fibres, irrespective of base used, is 2. Fibres dyed with reactive anthracenol in dry condition gives rubbing fastness in 3 to 4 (cotton) and 4 to 5 (wool) range. Beyond doubt it is clear that covalent bond formation improves the rubbing fastness.

3:5 SYNTHESIS OF REACTIVE DYES

Even though the discovery and successful application of reactive dyes is now more than two decade old, the know-how for the synthesis of reactive dyes is not easily available, since most information on reactive dyes is continued to patent literature. However, technical preparation of some of the commercial reactive dyes has been optimised and is described by Tilak et al. (101). The details of these are given by Pandit (102).

The techniques employed in the laboratory preparation and works manufacture of mono and dichlorotriazinyl dyes do not differ essentially from those in common use for making non-reactive acylated dyes. In order to avoid loss of reactivity, certain additional precautions are to be observed. For this reason, dichlorotriazinyl dyes are isolated in the cold from buffered solutions and dried in vacuo at the lowest convenient temperature in admixture with buffers to hinder autocatalytic hydrolysis.

As in other fields of dyestuff chemistry, it is often possible, at least in theory, to synthesise the same reactive triazinyl dye by more than one sequence of reactions. Other things being equal, the preferred sequence is usually that which gives rise to the fewest possible number of coloured products other than the desired one, or to such other coloured products as are most easily eliminated during isolation and subsequent purification; among the other products may be hydrolysed dye, so that it is implicit that the preferred sequence also be one that results in minimum hydrolysis.

Generally the dichloro-s-triazinyl dyes can be prepared by either of the following two routes:

(a) Preparation of an azo dye containing a free amino group and then condensing the azo dye with cyanuric chloride ;

(b) coupling a diazotized primary aromatic amine with a cyanurated coupling component.

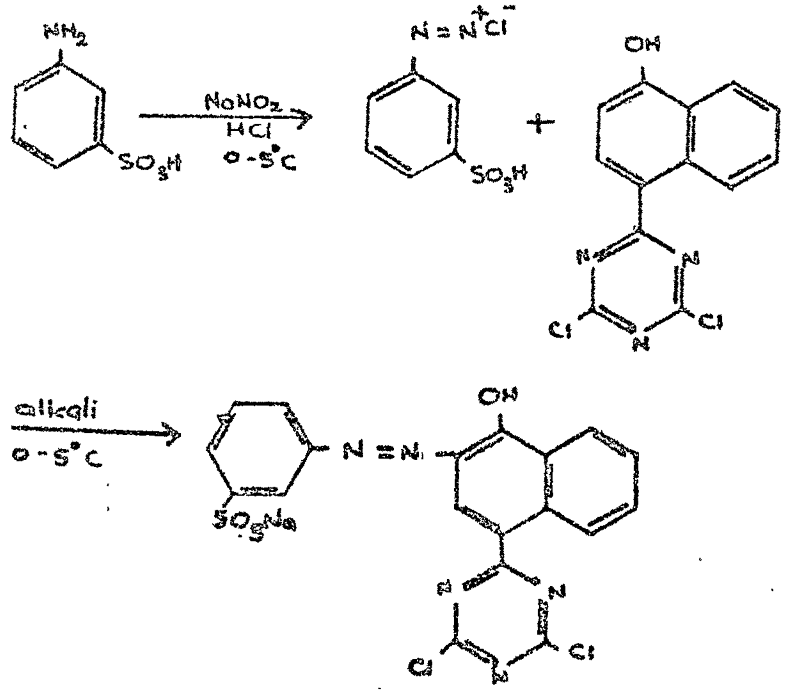
The choice of one of the above two routes depends mainly on the rate of the diazo-coupling reaction. If the coupling is very sluggish route (a) is preferred.

The aim of present investigation is to synthesis reactive dyes having -C-C-bridging system. It seems most unlikely to introduce reactive group with -C-C-bridge after preparing an azo dye. To synthesise such dyes route (b) seems most feasible. Three cyanurated coupling components, 2,4-dichloro-6-(4'-hydroxy-1'naphthyl)-s-triazine (Reactive Naphthol); 2,4-dichloro-6-(4'-hydroxy-1'-anthracenyl)-s-triazine (Reactive Anthracenol) and 2,4-dichloro-6-(8'-hydroxy-5'-quinolinyl)-s-triazine were prepared. Several amino aryl sulphonic acids were diazotized and coupled with them. Some representative examples are shown in schemes 2,3 and 4. The amino aryl sulphonic acids used are given in Tables 16,17,18.

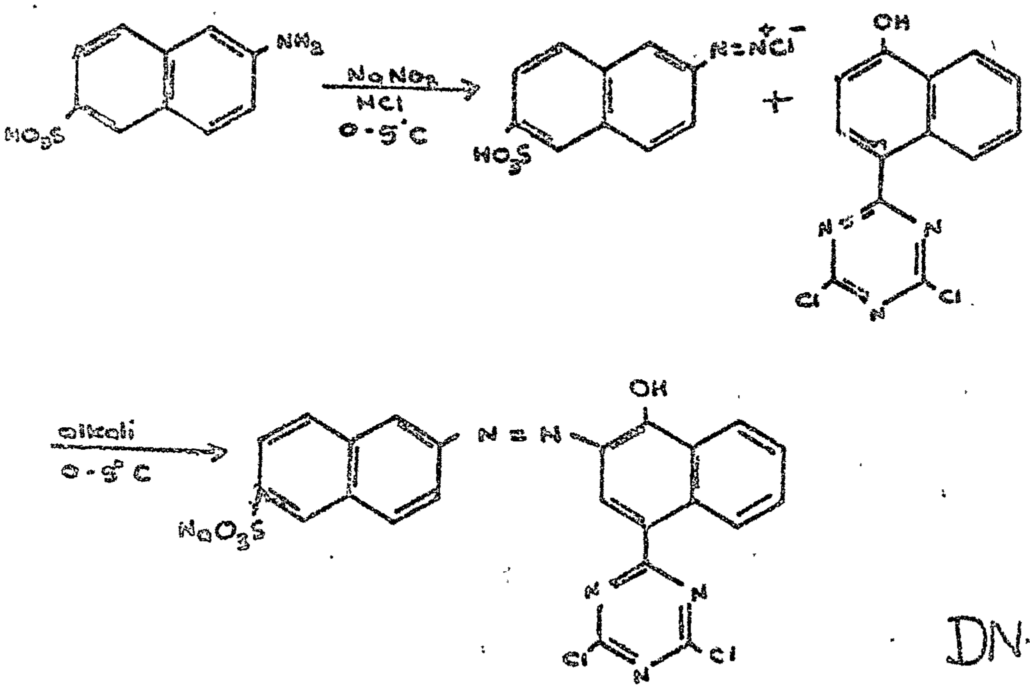
For storage purpose the dyes were mixed with 10% its weight of a mixture of anhydrous sodium dihydrogen

SCHEME : 2

3.5 SYNTHESIS OF REACTIVE DYES FROM REACTIVE NAPHTHOL



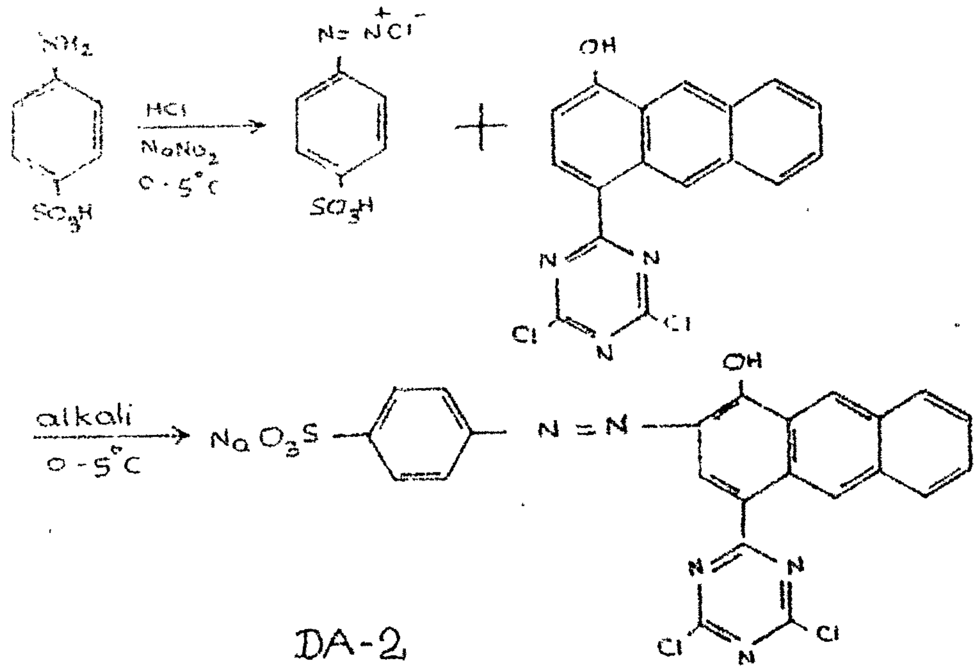
DN-1



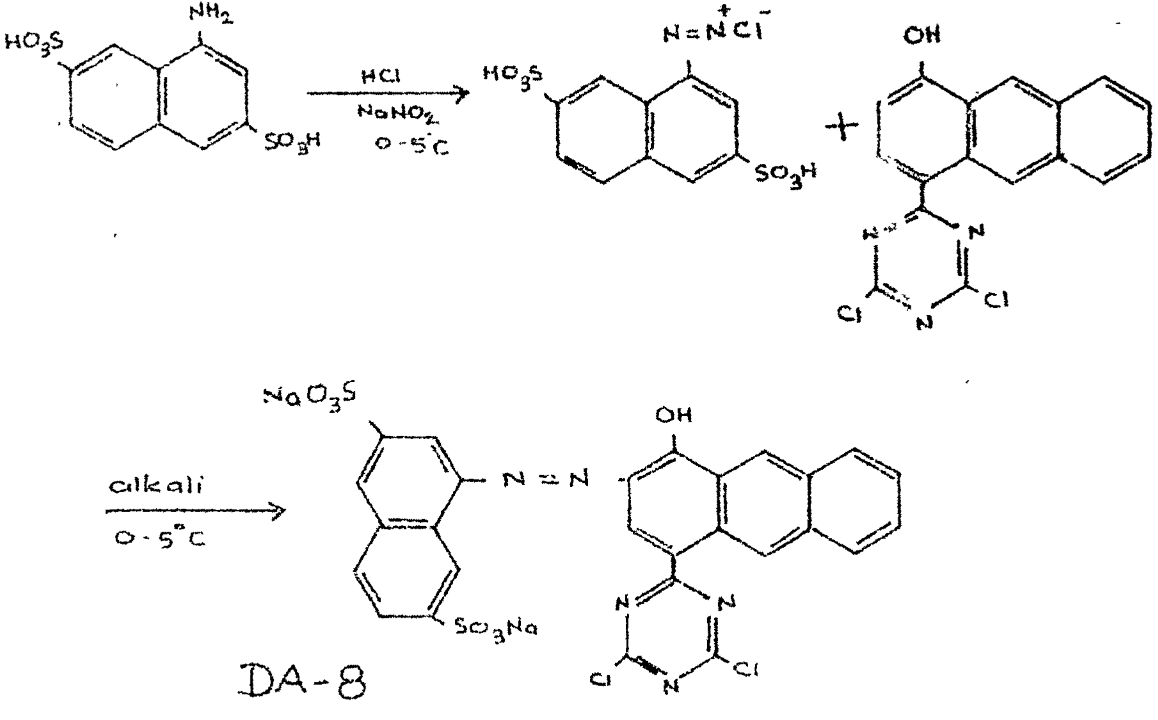
DN-7

SCHEME : 3

5.5 Synthesis Of Reactive Dyes From Reactive Anthracenol



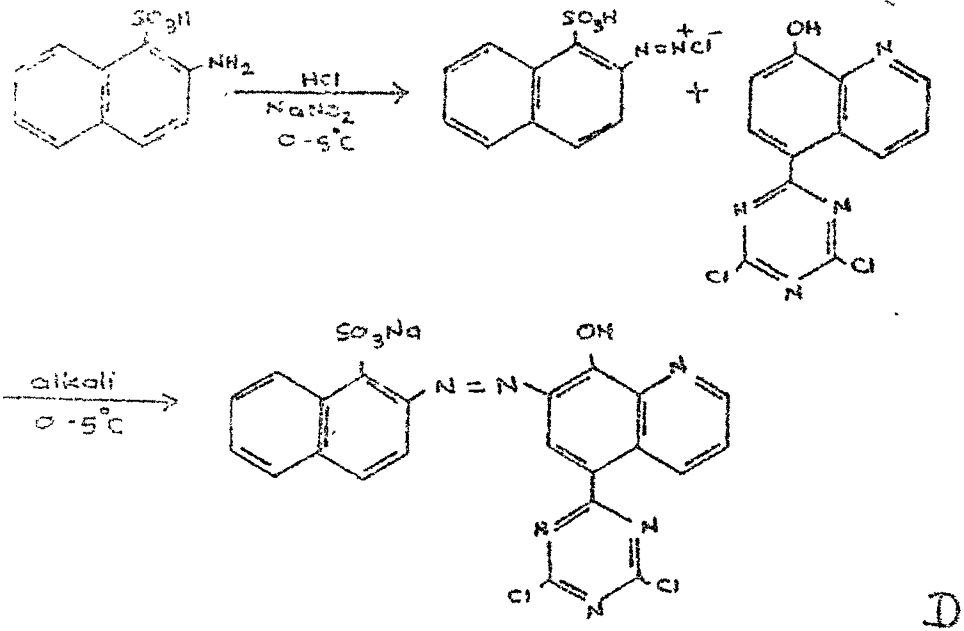
DA-2



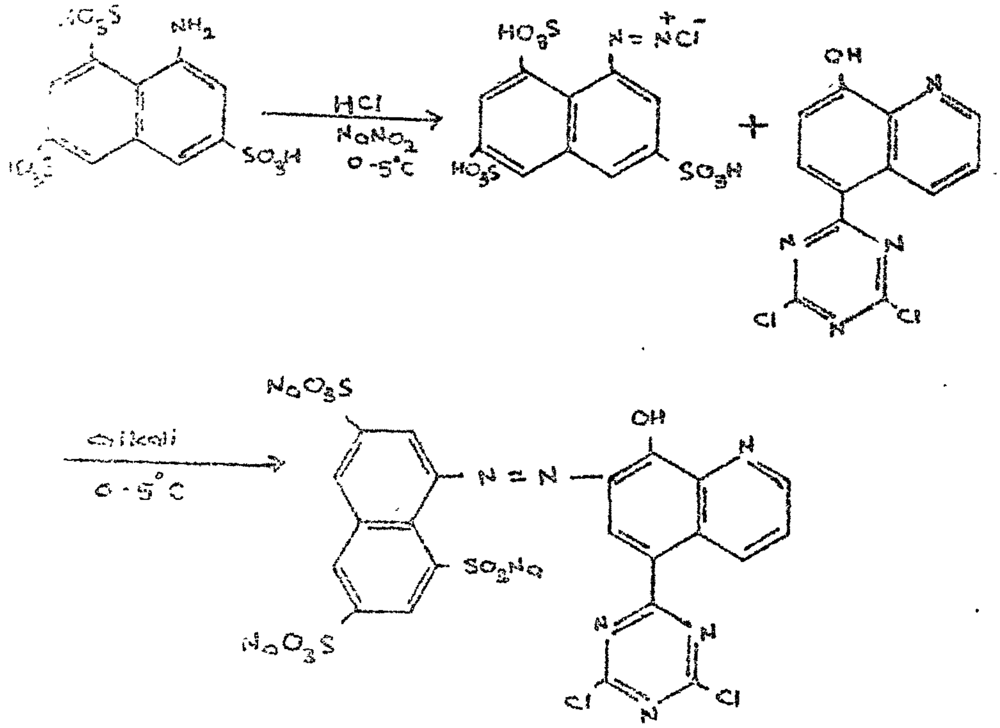
DA-8

SCHEME : 4

3.5 SYNTHESIS OF REACTIVE DYES FROM REACTIVE 8-HYDROXY QUINOLINE



DQ-3



DQ-10

TABLE 16

Reactive Dyes Prepared from Reactive Naphthol

No.	Amino aryl sulphonic acid	Dye No.	Mol. Formula	Analysis of Cl atoms	
				Found	Calculated
1	m-Amino benzene sulphonic acid	DN 1	$C_{19}H_{10}N_5Cl_2O_4S\,Na$	1.85	2.0
2	p-Amino benzene sulphonic acid	DN 2	$C_{19}H_{10}N_5Cl_2O_4SNa$	1.80	2.0
3	2-Amino naphthalene-1-sulphonic acid	DN 3	$C_{23}H_{12}N_5Cl_2O_4SNa$	1.75	2.0
4	1-Amino naphthalene-4-sulphonic acid	DN 4	$C_{23}H_{12}N_5Cl_2O_4SNa$	1.70	2.0
5	1-Amino naphthalene-6-sulphonic acid	DN 5	$C_{23}H_{12}N_5Cl_2O_4SNa$	2.10	2.0
6	1-Amino naphthalene-7-sulphonic acid	DN 6	$C_{23}H_{12}N_5Cl_2O_4SNa$	1.70	2.0
7	2-Amino naphthalene-6-sulphonic acid	DN 7	$C_{23}H_{12}N_5Cl_2O_4SNa$	1.60	2.0
8	1-Amino naphthalene-3,7-disulphonic acid	DN 8	$C_{23}H_{11}N_5Cl_2O_7S_2Na_2$	1.80	2.0
9	1-Amino naphthalene-4,8-disulphonic acid	DN 9	$C_{23}H_{11}N_5Cl_2O_7S_2Na_2$	2.10	2.0
10	1-Amino naphthalene-3,6,8-trisulphonic acid	DN 10	$C_{23}H_{10}N_5Cl_2O_{10}S_3Na_3$	1.80	2.0

TABLE 17

Reactive Dyes Prepared from Reactive Anthracenol

No.	Amino aryl sulphonic acid	Dye No.	Mol. Formula	Analysis of Cl atoms	
				Found	Calculated
1	m-Amino benzene sulphonic acid	DA-1	$C_{23}H_{12}N_5Cl_2O_4SNa$	1.70	2.0
2	p-Amino benzene sulphonic acid	DA-2	$C_{23}H_{12}N_5Cl_2O_4SNa$	1.90	2.0
3	2-Amino naphthalene-1-sulphonic acid	DA-3	$C_{27}H_{14}N_5Cl_2O_4SNa$	1.80	2.0
4	1-Amino naphthalene-4-sulphonic acid	DA-4	$C_{27}H_{14}N_5Cl_2O_4SNa$	1.70	2.0
5	1-Amino naphthalene-6-sulphonic acid	DA-5	$C_{27}H_{14}N_5Cl_2O_4SNa$	1.65	2.0
6	1-Amino naphthalene-7-sulphonic acid	DA-6	$C_{27}H_{14}N_5Cl_2O_4SNa$	1.80	2.0
7	2-Amino naphthalene-6-sulphonic acid	DA-7	$C_{27}H_{14}N_5Cl_2O_4SNa$	1.90	2.0
8	1-Amino naphthalene-3,7-disulphonic acid	DA-8	$C_{27}H_{13}N_5Cl_2O_7S_2Na_2$	1.70	2.0
9	1-Amino-naphthalene-4,8-disulphonic acid	DA-9	$C_{27}H_{13}N_5Cl_2O_7S_2Na_2$	1.60	2.0
10	1-Amino naphthalene-3,6,8-trisulphonic acid	DA-10	$C_{27}H_{12}N_5Cl_2O_{10}S_3Na_3$	2.0	2.0

TABLE 18

Reactive Dyes Prepared from Reactive 8-Hydroxyquinoline

No.	Amino aryl sulphonic acid	Dye No.	Mol.Formula	Analysis of Cl atoms Found	Analysis of Cl atoms Calculated
1	m-Amino benzene sulphonic acid	DQ-1	$C_{18}H_9N_6Cl_2O_4SNa$	1.60	2.0
2	p-Amino benzene sulphonic acid	DQ-2	$C_{18}H_9N_6Cl_2O_4SNa$	1.70	2.0
3	2-Amino naphthalene-1-sulphonic acid	DQ-3	$C_{22}H_{11}N_6Cl_2O_4SNa$	1.90	2.0
4	1-Amino naphthalene-4-sulphonic acid	DQ-4	$C_{22}H_{11}N_6Cl_2O_4SNa$	1.75	2.0
5	1-Amino naphthalene-6-sulphonic acid	DQ-5	$C_{22}H_{11}N_6Cl_2O_4SNa$	1.80	2.0
6	1-Amino naphthalene-7-sulphonic acid	DQ-6	$C_{22}H_{11}N_6Cl_2O_4SNa$	1.80	2.0
7	2-Amino naphthalene-6-sulphonic acid	DQ-7	$C_{22}H_{11}N_6Cl_2O_4SNa$	1.90	2.0
8	1-Amino naphthalene-3,7-disulphonic acid	DQ-8	$C_{22}H_{10}N_6Cl_2O_7S_2Na_2$	1.80	2.0
9	1-Amino naphthalene-4,8-disulphonic acid	DQ-9	$C_{22}H_{10}N_6Cl_2O_7S_2Na_2$	1.65	2.0
10	1-Amino naphthalene-3,6,8-trisulphonic acid	DQ-10	$C_{22}H_9N_6Cl_2O_{10}S_3Na_3$	1.80	2.0

phosphate and anhydrous disodium hydrogen phosphate. The dyes buffered in such a way, greately retards the hydrolysis (103,104).

For purifying the reactive dyes, the method reported by Robinson and Mills is generally used (105). In this method, the dye is dissolved in water and is reprecipitated using sodium acetate or potassium acetate. The excess of sodium or potassium acetate remain in dye is then extracted with ethanol. Now a days the method used is to dissolve the dye in dimethylformamide, filtered and precipitated with acetone or chloroform (106,107). The various aspects of this method is discussed by Chavan (108). Recently Datyner and co-workers have purified reactive dyes by recrystallizing from a mixture of water-ethanol (99). For our work, we have followed the solvent-non-solvent technique to purify the reactive dyes.

The purity of the reactive dyes was checked by thin layer chromatography. Sramek has used descending technique on Whatman No.1 paper with pyridine-amyl alcohol -ammonia (1.3:1:1) mixture (109), while Kuypers and Kiel has used 25% ammonium hydroxide as mobile phase (110). The paper chromatographic behaviour of Remazol reactive dyes has been studied by Caldwell et al (111) and Rf values of reactive dyes available in East Germany are reported by Reif (112). The Rf values of Procion, Cibacron, Reactone, Drimarene X and Z, Primarin, Remazol, Levafix and Levafix E dyes are determined by ascending chromatography (113). Different eluent solvent mixtures are used for resolution of these dyes. As reactive dyes have high substantivity for cellulose, in paper chromatography, large interference and restraint on the migration of reactive dyes is arised. In thin layer chromatography no such interference arises. Perkavac and Perpar have studied thin layer chromatography on silica gel with different solvent mixtures for several reactive dyes (114). Recently Sherial et al. have used barium sulphate for preparation of TLC plates and reported Rf values of reactive dyes (115). It was observed that better separation can be done by thin-layer chromatography than the paper chromatography.

After purifying the reactive dyes, these were subjected to determine hydrolyzable chlorine atoms per molecule. A direct method based on the potentiometric determination of the ionic chlorine of hydrolysed dye solution with 0.01 N silver nitrate was used (116).

The number of reactive chlorine was also determined by means of titration of the alkali consumption of a dyestuff solution of known molar solutions at a constant pH. The average of chlorine atoms determined by both the methods is given in Tables 16-19. It is observed that they are in good agreement with the calculated one.

3:5:1 Synthesis of Disazo Reactive Dyes

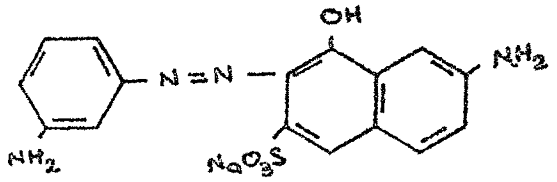
It is a well known fact that increase in molecular weight of naphthols in azoic dyeing by increasing the complexity of the fused ring systems in naphthols leads to greater substantivity and also has a bathochromic effect. So for getting higher shades, attempt was made to utilize anthracenol moity. Reactive anthracenol was used for reactive azoic dyeing as well as for synthesising reactive dyes. Eventhough the desired shift in the colour was not obtained. For obtaining higher shades disazo dyes are used (117). Several patents are appeared claiming the blue disazo reactive dyes (118-122). With a view to obtain dyes having higher shades. Synthesis of disazo reactive dyes was carried out.

Eight diazo components were synthesised. These are listed in Chart-1. These were synthesised by diazotising

CHART - 1

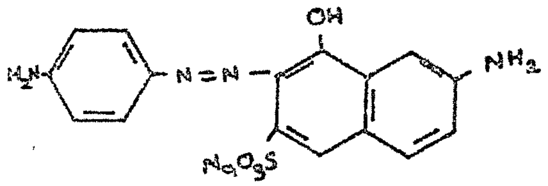
DIAZO COMPONENTS

(i)



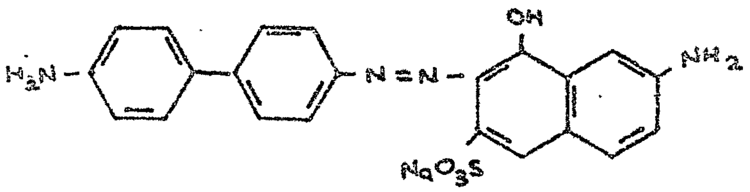
C-1

(ii)



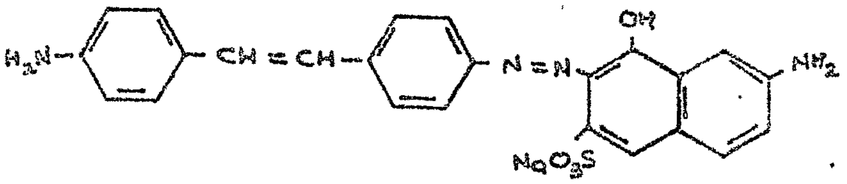
C-2

(iii)



C-3

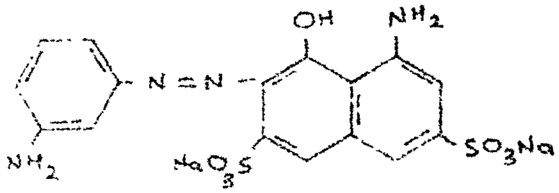
(iv)



C-4

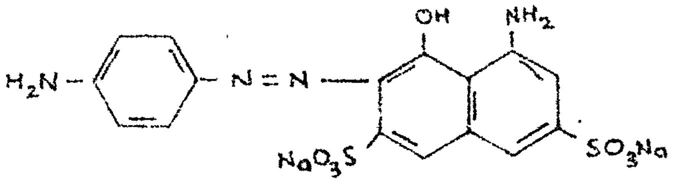
(cont.)

(v)



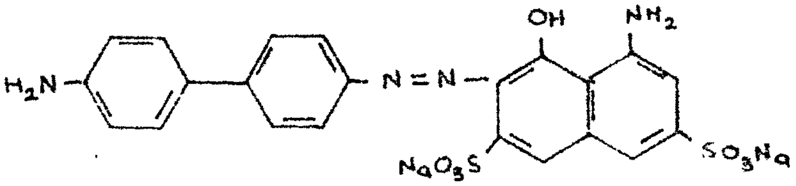
C-5

(vi)



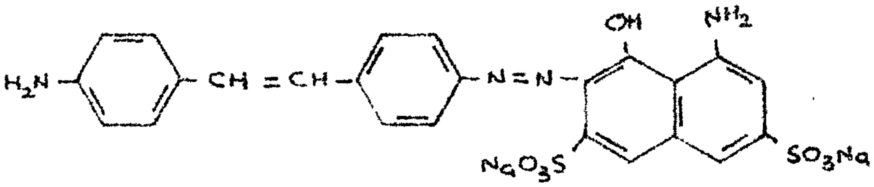
C-6

(vii)



C-7

(viii)



C-8

TABLE 19

Reactive Disazo Dyes Prepared from Reactive Naphthol

No.	Diazo component	Dye No.	Mol. Formula	Analysis of Cl atoms Found	Analysis of Cl atoms Calculated
1	C-1	DDN-1	$C_{29}H_{17}N_8O_5Cl_2SNa$	1.65	2.0
2	C-2	DDN-2	$C_{29}H_{17}N_8O_5Cl_2SNa$	1.75	2.0
3	C-3	DDN-3	$C_{35}H_{21}N_8O_5Cl_2SNa$	1.90	2.0
4	C-4	DDN-4	$C_{37}H_{21}N_8O_{11}Cl_2S_3Na_3$	1.60	2.0
5	C-5	DDN-5	$C_{29}H_{16}N_8O_8Cl_2S_2Na_2$	1.70	2.0
6	C-6	DDN-6	$C_{29}H_{16}N_8O_8Cl_2S_2Na_2$	1.70	2.0
7	C-7	DDN-7	$C_{35}H_{20}N_8O_8Cl_2S_2Na_2$	1.85	2.0
8	C-8	DDN-8	$C_{37}H_{20}N_8O_{14}Cl_2S_4Na_4$	1.80	2.0

TABLE 20

Reactive Disazo Dyes Prepared from Reactive Anthracenol

No.	Diazo component	Dye No.	Mol. Formula	Analysis of Cl atoms Found	Analysis of Cl atoms Calculated
1	C-1	DDA-1	$C_{33}H_{19}N_8O_5Cl_2SNa$	1.60	2.0
2	C-2	DDA-2	$C_{33}H_{19}N_8O_5Cl_2SNa$	1.80	2.0
3	C-3	DDA-3	$C_{39}H_{23}N_8O_5Cl_2SNa$	1.55	2.0
4	C-4	DDA-4	$C_{41}H_{23}N_8O_{51}Cl_2S_3Na_3$	1.60	2.0
5	C-5	DDA-5	$C_{33}H_{18}N_8O_8Cl_2S_2Na_2$	1.60	2.0
6	C-6	DDA-6	$C_{33}H_{18}N_8O_8Cl_2S_2Na_2$	1.65	2.0
7	C-7	DDA-7	$C_{39}H_{22}N_8O_8Cl_2S_2Na_2$	1.65	2.0
8	C-8	DDA-8	$C_{41}H_{22}N_8O_{14}Cl_2S_4Na_4$	1.80	2.0

TABLE 21

Reactive Disazo Dyes Prepared from Reactive 8-Hydroxyquinoline

No.	Diazo component	Dye No.	Mol.Formula	Analysis of Cl atoms	
				Found	calculated
1	C-1	DDQ-1	$C_{28}H_{16}N_9O_5Cl_2SNa$	1.90	2.0
2	C-2	DDQ-2	$C_{28}H_{16}N_9O_5Cl_2SNa$	1.80	2.0
3	C-3	DDQ-3	$C_{34}H_{20}N_9O_5Cl_2SNa$	1.75	2.0
4	C-4	DDQ-4	$C_{36}H_{20}N_9O_{11}Cl_2S_3Na_3$	1.60	2.0
5	C-5	DDQ-5	$C_{28}H_{15}N_9O_8Cl_2S_2Na_2$	1.70	2.0
6	C-6	DDQ-6	$C_{28}H_{15}N_9O_8Cl_2S_2Na_2$	1.90	2.0
7	C-7	DDQ-7	$C_{34}H_{19}N_9O_8Cl_2S_2Na_2$	1.70	2.0
8	C-8	DDQ-8	$C_{36}H_{19}N_9O_{14}Cl_2S_4Na_4$	1.85	2.0

TABLE 22

Visible Spectra of Monoazo Dyes Derived From Reactive Naphthol

No.	Dye No.	Absorption Maxima in DMF nm	Absorption Maxima in water nm
1	DN-1	510	505
2	DN-2	515	510
3	DN-3	540	535
4	DN-4	545	535
5	DN-5	535	520
6	DN-6	540	525
7	DN-7	545	530
8	DN-8	540	530
9	DN-9	550	535
10	DN-10	545	530

TABLE 23

Visible Spectra of Monoazo Dyes Derived from Reactive Anthracenol

No.	Dye No.	Absorption Maxima in DMF	Absorption Maxima in water
1	DA-1	530	520
2	DA-2	540	530
3	DA-3	550	545
4	DA-4	560	550
5	DA-5	550	535
6	DA-6	560	540
7	DA-7	565	545
8	DA-8	560	555
9	DA-9	565	550
10	DA-10	560	545

TABLE 24

Visible Spectra of Monoazo Dyes Derived from Reactive 8-hydroxy quinoline

No.	Dye No.	Absorption Maxima	
		in DMF	in water
1	DQ-1	480	470
2	DQ-2	490	475
3	DQ-3	510	505
4	DQ-4	525	515
5	DQ-5	515	510
6	DQ-6	510	500
7	DQ-7	520	505
8	DQ-8	505	500
9	DQ-9	525	515
10	DQ-10	520	505

TABLE 25

Visible Spectra of Disazo Dyes Dervied from Reactive Naphthol

No.	Dye No.	Absorption Maxima	
		in DMF	in water
1	DDN-1	550	540
2	DDN-2	560	550
3	DDN-3	570	565
4	DDN-4	580	570
5	DDN-5	570	565
6	DDN-6	580	570
7	DDN-7	580	570
8	DDN-8	590	585

TABLE 26

Visible Spectra of Disazo Dyes Derived from Reactive Anthracenol

No.	Dye No.	Absorption Maxima	
		in DMF	in Water
1	DDA-1	570	555
2	DDA-2	580	570
3	DDA-3	580	575
4	DDA-4	590	580
5	DDA-5	590	575
6	DDA-6	600	590
7	DDA-7	605	590
8	DDA-8	610	590

TABLE 27

Visible Spectra of Disazo Dyes Derived from Reactive 8-hydroxy quinoline

No.	Dye No.	Absorption Maxima	
		in DMF	in Water
1	DDQ-1	535	525
2	DDQ-2	540	530
3	DDQ-3	555	540
4	DDQ-4	560	550
5	DDQ-5	545	540
6	DDQ-6	550	545
7	DDQ-7	565	555
8	DDQ-8	575	560

the band shifts to the longer wavelength viz.

Benzene $<$ Naphthalene $<$ Anthracene

λmax 183 $<$ 220 $<$ 255

Similarly the monoazo dyes possessing the benzene ring in the diazo component (i.e. dyes DN-1, DN-2; DA-1, DA-2 and DQ-1, DQ-2) have the lowershift in λmax as compared to the naphthalene ring (i.e. dyes DN-3 to DN-10; DA-3 to DA-10 and DQ-3 to DQ-10). Also from the comparision of the dyes derived from the reactive naphthol (DN and DDN dyes) and reactive anthracenol (DA and DDA dyes), it revels that the later dyes have bathochromic shift. Thus as the number of condensed ring increases in the benzene series, the absorption, λmax, moves progressively to longer wavelength. The introduction of the hetero atom produces a marked hypsochromic and hyperchromic effect on the wavelength of maximum absorption (19). The dyes derived from reactive 8-hydroxy quinoline have the λmax at the shorter wavelength (hypsochromic) compared to the dyes derived from naphthol and anthracenol. This may be due to the hetero atom which has the hyperchromic effect (19).

The increase in conjugation and double bond have the bathochromic shift (9). In the present study, the disazo dyes are having λmax at higher wavelength as compared to monoazo dyes, confirms the above statement.

The wavelength and intensity of the absorption bands are affected when a molecule is in a solvent environment compared with its spectrum in the gas phase. This is due to the unequal perturbation of the ground and excited electronic states of the molecule which depends on the nature of the solvent-solute interaction in two states.

It is an established fact that the fine structure of absorption curves and the intensities of bands are affected by the nature of solvent used for spectroscopic examination. In general, with increasing solvent polarity the spectra suffers a loss of vibrational fine structure because of strong solute interaction in highly polar solvents especially when solute molecules possess induced or permanent dipole characteristics.

Owing to [illegible] insolubility of reactive dyes in common organic solvents viz. acetone, alcohol, chloroform, carbon tetrachloride, diethyl ether etc. the spectra could not be recorded in different solvents except water and dimethyl formamide. In both the solvents the peaks are broad and with the increase of the dielectric constant (D), the peak shifts to shorter wavelength.

Order of λmax $\qquad$ DMF $>$ Water

Order of D $\qquad$ DMF $<$ Water

It is premature at this stage to offer a suitable explanation for such behaviour unless quantitative studies are made with other solvents of varying polarity. Besides the usual solvent-solute interactions, the acid-base equilibria, producing different absorbing species (both molecular and anionic), should be responsible for the changes in spectra. In literature, both bathochromic and hypsochromic displacements of bands with solvent have been recorded with different categories of aromatic compounds. Even for the same compound the direction of the solvent shifts has not always been the same for all absorption bands (124,125).

3.7 INFRA RED SPECTRA OF REACTIVE DYES

Some representative dyes were subjected for i.r. spectra. In the i.r. spectra of dyes only the most predominant peaks are assigned for their characterisation. A broad and weak band is observed for 3200-3000 cm^{-1} range. This may be assigned for intramolecular -OH group (126). The peak due to N=N is generally found around 1450-1400 cm^{-1} region (127). In the present investigation peaks around this region is obtained, confirming the -N=N- group. Ofcourse, in some cases, this band was observed in 1500 cm^{-1} region. The peak due to C=N group is assigned with uncertaintity around 1665 cm^{-1}.

3.8 DYEING OF COTTON

It is not intended to describe here the different methods of application of reactive dyes of cotton, because excellent technical literature on this subject has been published by most leading dyestuff manufacturers in the form of dyeing manuals and pattern cards and have been discussed by Rattee (128) and by Fowler and Marshall (129). For cellulose dyeing several papers have been published concerning the use of individual commercial ranges, viz. Procion (ICI) (130), Levafix (BAY) (131) Drimarene (S) (132), Remazol (FH) (133), and Primazin (BASF) (134) dyes, for various dyeing processes, especially vinyl-sulphone (Remazol) (135) and halogenotriazine reactive dyes (136) for exhaustion methods (137), Remazol (FH) dyes for the pad-short dwell process (137) and Drimarene R and K (S) dyes for the cold batch dyeing process (139). In the present investigation the general process used for dyeing was same as that used for dichloro-s-triazine dyes. Under this condition the dyeability of the dyes were found to be good to excellent grades. Uniform and level dyeing was obtained. The shades obtained with these dyes are given in Tables 28-33. The full range of shades i.e. from orange to blue shades are obtained. The monoazo dyes synthesised from reactive naphthol (DN dyes) are giving shades of red to violet range, while monoazo dyes prepared from reactive anthracenol (DA dyes) is producing reddish violet shades. The monoazo dyes derived from 8-hydroxy quinoline (DQ-series) dyes fibres in orange to red shades. As expected the disazo

TABLE 28

Shade Obtained on Cotton and Fastness Properties of Monoazo Dyes Derived from Reactive Naphthol

No.	Dye No.	Shade	Washing Fastness		Light Fastness
			ISO No.4	ISO No.5	
1	DN-1	Red	5	5	5-6
2	DN-2	Red	5	5	6
3	DN-3	Reddish Violet	5	5	6
4	DN-4	Reddish Violet	5	5	6
5	DN-5	Dark Red	5	5	5-6
6	DN-6	Reddish Violet	5	5	5-6
7	DN-7	Light Violet	5	5	5
8	DN-8	Reddish Violet	5	5	5
9	DN-9	Violet	5	5	5
10	DN-10	Reddish Violet	5	5	5-6

TABLE 29

Shade Obtained on Cotton and Fastness Properties of Monoazo Dyes Prepared from Reactive Anthracenol

No.	Dye No.	Shade	Washing Fastness		Light Fastness
			ISO No. 4	ISO No. 5	
1	DA-1	Reddish Violet	5	5	4-5
2	DA-2	Reddish Violet	5	5	5
3	DA-3	Violet	5	5	4-5
4	DA-4	Violet	5	5	5
5	DA-5	Light Violet	5	5	4
6	DA-6	Reddish Violet	5	5	4-5
7	DA-7	LightViolet	5	5	4
8	DA-8	Violet	5	5	4
9	DA-9	Violet	5	5	3-4
10	DA-10	Reddish Violet	5	5	4

TABLE 30

Shade Obtained on Cotton and Fastness Properties of Monoazo Dyes Prepared from Reactive 8-Hydroxy quinoline

No.	Dye No.	Shade	Washing Fastness ISO No. 4	Washing Fastness ISO No. 5	Light Fastness
1	DQ-1	Orange	4-5	4	5
2	DQ-2	Orange	4-5	4	5-6
3	DQ-3	Red	5	4-5	5-6
4	DQ-4	Red	5	5	6
5	DQ-5	Red	5	5	5-6
6	DQ-6	Red	5	4-5	5
7	DQ-7	Red	4-5	4	4-5
8	DQ-8	Red	5	5	4-5
9	DQ-9	Red	5	5	5
10	DQ-10	Orange	4-5	4-5	5

TABLE 31

Shade Obtained on Cotton and Fastness Properties of Disazo Dyes Prepared from Reactive Naphthol

No.	Dye No.	Shade	Washing Fastness ISO No.4	Washing Fastness ISO No.5	Light Fastness
1	DDN-1	Reddish violet	5	4-5	5-6
2	DDN-2	Reddish violet	5	4-5	6
3	DDN-3	Violet	5	4-5	5-6
4	DDN-4	Violet	5	4	6
5	DDN-5	Reddish Violet	5	4-5	6
6	DDN-6	Violet	5	4-5	5-6
7	DDN-7	Violet	5	4-5	5-6
8	DDN-8	Reddish blue	5	4	6

TABLE 32

Shade Obtained on Cotton and Fastness Properties of Disazo Dyes Prepared from Reactive Anthracenol

No.	Dye No.	Shade	Washing Fastness		Light Fastness
			ISO No.4	ISO No.5	
1	DDA-1	Reddish violet	5	4-5	4
2	DDA-2	Violet	5	4-5	4
3	DDA-3	Violet	5	4-5	4
4	DDA-4	Blue	4-5	4	4-5
5	DDA-5	Reddish Blue	5	4-5	4-5
6	DDA-6	Blue	4-5	4	4
7	DDA-7	Blue	4-5	4	4
8	DDA-8	Blue	4-5	4	4-5

TABLE 33

Shade Obtained on Cotton and Fastness Properties of Disazo Dyes Prepared from Reactive 8-Hydroxyquinoline .

No.	Dye No.	Shade	Washing Fastness		Light Fastness
			ISO No. 4	ISO No.5	
1	DDQ-1	Reddish violet	4-5	4	5
2	DDQ-2	Reddish violet	4-5	4	5-6
3	DDQ-3	Reddish violet	4-5	4	5
4	DDQ-4	Violet	4	4	5
5	DDQ-5	Light violet	4-5	4	4-5
6	DDQ-6	Violet	4-5	4	5
7	DDQ-7	Reddish violet	4-5	4	4-5
8	DDQ-8	Violet	4	4	4-5

dyes are producing higher shades. Reddish violet to reddish blue shades are obtained from disazo dyes of reactive naphthol series (DDN-series), while reddish violet to blue shades are obtained from disazo dyes of reactive anthracenol series (DDA-series). The disazo dyes prepared from reactive 8-hydroxy quinoline (DDQ-series) produce reddish violet to violet shades. Thus it is clear that DDA dyes give highest shades and DQ dyes produce lightest shades. The shades obtained from different series can be generalised in order as

$$\mathrm{DDA} > \mathrm{DDN} > \mathrm{DDQ} > \mathrm{DA} > \mathrm{DN} > \mathrm{DQ} .$$

The conclusion derived from the shades obtained is that the increase in fused ring system in coupling component leads to a bathochromic shift (e.g. comparision of DA and DN, DDA and DDN dyes), while introduction of a hetero atom in naphthalene nucleus has a reverse effect (e.g. comparision of DN and DQ, DDN and DDQ series).

3.8.1 Washing Fastness

The washing fastness of the dyed fibres is given in Tables 28-33. The washing fastness of the fibres are in 4 to 5 range. The monoazo-dyes prepared from reactive naphthol and reactive anthracenol gives washing fastness of highest grade, while reactive 8-hydroxy quinoline monoazo dyes (DQ dyes) have some lower washing fastness. In case of disazo dyes synthesised from reactive naphthol and reactive anthracenol (DDN and DDA dyes) dyes cotton with washing fastness of 4 to 5 range. Here also the disazo dyes of 8-hydroxy quinoline show some less washing fastness as compared to other two series of disazo dyes. From the comparision of washing fastness of monoazo and disazo dyes synthesised from the same coupling components (i.e. comparision between DN and DDN; DA and DDA and DQ and DDQ) it is revealed that monoazo dyes are having more washing fastness than disazo dyes.

Generally the available commercial reactive dyes possess high wet fastness. The importance of reactive dyes lie in its high washing fastness. In the present investigation the synthesised reactive dyes give high wet fastness. Thus these dyes can stand well with the available dyes.

3.8.2 Light Fastness

The light fastness of the cotton fibres are reported in Tables 28-33. Approximately the light fastness of these series can be given in the following decreasing order:

$$\mathrm{DDN} > \mathrm{DN} > \mathrm{DDQ} > \mathrm{DQ} > \mathrm{DDA} > \mathrm{DA}$$

It is clear from this order that the introduction of fused ring system in the coupling component (i.e. from reactive naphthol to reactive anthracenol) decreases the light fastness markably while only some decrease is observed when hetero atom is introduced in coupling component (i.e. reactive naphthol to reactive 8-hydroxy quinoline).

3.9 WOOL DYEING

The reaction of wool with dyes of the chlorotriazine type can be represented as follows:

$$\textcircled{\mathrm{D}}-\mathrm{Cl} + \mathrm{Wool{-}NH_2} \longrightarrow \mathrm{Dye} - \mathrm{NH} - \mathrm{Wool} + \mathrm{HCl}$$

Thus reaction can occur with terminal and side-chain amino groups with the -SH of cysteine and with the hydroxyl group of the tyrosine residue (140). The cysteine is highly reactive, but unless the wool has undergone a reducing treatment the number of -SH groups present will be very less. The most abundant groups are the side-chain amino groups, especially those of the lysine residues, and it is with these groups that reaction mainly takes place under normal dyeing conditions (141). The distribution of the reactive dye molecules between the different groups will vary for different experimental conditions. The behaviour of chloroacetyl, omega-chloroalkylsulphonamide, vinyl sulphone, chlorotriazinyl, chloropyrimidyl dyes as well as of dyes containing acrylamido groups with wool has been studied (142). Recently Altenhofen and Zahn have reported reactions of difluorochloropyrimidine dyestuff with wool peptide models (143).

In practice the application of reactive dyes to wool is much less straightforward than their application to cellulosic fibres, the following difficulties being encountered

(i) Unlevel dyeing

(ii) Inadequate reaction with the fibre in the weakly acidic range suitable for dyeing wool

(iii) The problem of removing hydrolysed and unreacted dye at the completion of dyeing.

Apart from any question of fibre selectivity, the first consideration with any type of dye is to obtain even absorption and with reactive dyes this requires careful control of temperature. In respect of pH, reactive dyes behave like milling acid dyes, the appropriate dyebath pH being about 5. At lower pH values, e.g. at pH 3, dyeing is uneven with poor fixation and at higher pH e.g. pH 7, there is poor exhaustion. The rate of reaction of dye with the fibre increases with increasing pH, but very rapid reaction causes unlevel dyeing because reacted dye cannot migrate. The rate of reaction at the boil is usually adequate at about pH 5. With the newly synthesised dye the additional advantage observed at pH 5 was the minimum hydrolysis in this region.

After dyeing the wool fibres, the hydrolysed and unreacted dye was removed. Numerous studies have been carried out and various methods are proposed for this purpose. The major methods used are:

(i) 25% pyridine at boil (144)

(ii) 50% urea plus 1% dispersol VL at the boil or at 60°C (145, 146)

(iii) acid pyridine (10 parts pyridine, 20 parts formic acid (90%) and 70 parts water) at the boil (147);

(iv) hot neutral pyridine (49.9 parts pyridine, 49.9 parts water and 0.2 parts HCl (35.5%) (148).

Datyner et al. have used a method involving buffered solutions of urea and a cationic-nonionic surfactant in order to determine fixation ratios (149). The method is claimed to be satisfactory for difluorochloropyrimidine dyes, the dye-wool bond being stable under their extraction conditions. Recently Asquith and co-workers have compared these methods and found that acid pyridine is most efficient and gives satisfactory results (150). In our present work this method was used.

3:9:1 Shade obtained

The shades obtained on wool fibres are given in Tables 34-39. The wide range of shades are obtained varied from red to blue. The shades are uniform and bright in colour. The monoazo dyes synthesised from reactive naphthol produce red to violet shades while the monoazo dyes prepared from reactive anthracenol give some higher shades of violet range. Only red shade is obtained from monoazo dyes of reactive 8-hydroxy quinoline. Relative to monoazo dyes

TABLE 34

Shade Obtained on Wool and Fastness Properties of Monoazo Dyes Prepared from Reactive Naphthol

No.	Dye No.	Shade	Washing Fastness ISO No.3	 ISO No.4	Light Fastness
1	DN-1	Red	5	5	6
2	DN-2	Red	5	5	6
3	DN-3	Light violet	5	5	6
4	DN-4	Reddish violet	5	5	6
5	DN-5	Reddish violet	5	5	6
6	DN-6	Light violet	5	5	6
7	DN-7	Violet	5	5	6
8	DN-8	Violet	5	5	6
9	DN-9	Brown	5	5	6
10	DN-10	Brown	5	5	6

TABLE 35

Shade Obtained on Wool and Fastness Properties of Monoazo Dyes Prepared from Reactive Anthracenol

No.	Dye No.	Shade	Washing Fastness		Light Fastness
			ISO No. 3	ISO No. 4	
1	DA-1	Brown	5	5	5
2	DA-2	Brown	5	5	5
3	DA-3	Violet	5	5	5
4	DA-4	Violet	5	5	5
5	DA-5	Violet	5	5	4-5
6	DA-6	Violet	5	5	5
7	DA-7	Brown	5	5	4-5
8	DA-8	Violet	5	5	4-5
9	DA-9	Brown	5	5	4
10	DA-10	Brown	5	5	4-5

TABLE 36

Shade Obtained on Wool and Fastness Properties of Monoazo Dyes Prepared from Reactive 8-Hydroxyquinoline

No.	Dye No.	Shade	Washing Fastness ISO No. 3	 ISO No. 4	Light Fastness
1	DQ-1	Red	5	4-5	5
2	DQ-2	Red	5	4	6
3	DQ-3	Red	5	5	6
4	DQ-4	Red	5	4-5	6
5	DQ-5	Red	5	5	6
6	DQ-6	Red	5	5	5-6
7	DQ-7	Red	5	4-5	5
8	DQ-8	Red	5	4-5	6
9	DQ-9	Red	5	5	5-6
10	DQ-10	Red	5	5	6

TABLE 37

Shade Obtained on Wool and Fastness Properties of Disazo Dyes Prepared from Reactive Naphthol

No.	Dye No.	Shade	Washing Fastness ISO No. 3	Washing Fastness ISO No. 4	Light Fastness
1	DDN-1	Violet	5	5	6
2	DDN-2	Dark violet	5	5	6
3	DDN-3	Light blue	5	5	6
4	DDN-4	Light blue	5	5	6
5	DDN-5	Violet	5	5	6
6	DDN-6	Blue	5	5	6
7	DDN-7	Blue	5	5	6
8	DDN-8	Blue	5	5	6

TABLE 38

Shade Obtained on Wool and Fastness Properties of Disazo Dyes Prepared from Reactive Anthracenol

No.	Dye No.	Shade	Washing Fastness		Light Fastness
			ISO No. 3	ISO No. 4	
1	DDA-1	Blue	5	5	4-5
2	DDA-2	Blue	5	5	5
3	DDA-3	Blue	5	5	4-5
4	DDA-4	Blue	5	5	4-5
5	DDA-5	Blue	5	5	5
6	DDA-6	Blue	5	5	4-5
7	DDA-7	Greenish blue	5	5	4
8	DDA-8	Greenish blue	5	5	4-5

TABLE 39

Shade Obtained on Wool and Fastness Properties of Disazo Dyes Prepared from Reactive 8-Hydroxyquinoline

No.	Dye No.	Shade	Washing Fastness		Light Fastness
			ISO No. 3	ISO No. 4	
1	DDQ-1	Reddish violet	5	4	5
2	DDQ-2	Reddish violet	5	4-5	6
3	DDQ-3	Violet	5	4-5	5-6
4	DDQ-4	Violet	4-5	4	6
5	DDQ-5	Violet	5	5	5
6	DDQ-6	Violet	5	4-5	5
7	DDQ-7	Violet	5	4	5
8	DDQ-8	Violet	5	4-5	5

disazo dyes are producing higher shades. The disazo dyes synthesised from all the three reactive coupling components are giving violet to blue colours. Compare to cotton fibres, very little change in shade is observed.

3:9:2 Washing Fastness

Washing fastness of all fibres are of highest grade, only in few cases of 4-5 range is obtained. This is shown in Tables 34-39.

3:9:3 Light Fastness

Light fastness of dyed wool fibres are tabulated in Tables 34-39. The monoazo and disazo dyes synthesised from reactive naphthol give light fastness 6, while the dyes synthesised from reactive 8-hydroxy quinoline show light fastness in 5 to 6 range. Reactive anthracenol dyes, monoazo and disazo, possess some less light fastness, in 4 to 5 range. Generally the following increasing light fastness trend is observed

$$\mathrm{DDA} \simeq \mathrm{DA} < \mathrm{DDQ} < \mathrm{DQ} < \mathrm{DDN} = \mathrm{DN}$$

The comparision of light fastness of cotton fibres and wool fibres dyed with the same dye indicate that wool fibres are having more light fastness as compared to cotton fibres. Similar behaviour was observed in reactive azoic dyeing also.

3:10 SOLVENT DYEING

Very little information is available on dyeing of cellulose fibres from solvents. Although organic solvents are in fairly widespread use in textile finishing, they are still only in their infancy as processing media. The advantages of solvent dyeing are mainly determined by the following factors:

(i) cost of water and effluent-disposal problems
(ii) economics of heat
(iii) technical effects

The water requirements of the textile industry are comparatively high, so that the cost of fresh water is an important factor to textile dyeing and finishing organizations. Furthermore, effluent treatment is also expensive. Although it is fairly simple, technically, disposal regulations are becoming progressively stricter.

The thermo-economics of organic solvents are determined in particular by a fairly low specific heat and a fairly low heat of vaporisation. Recently a paper on tentative comparision of aqueous- and non-queous processes on a time and cost basis have been published (151, 152).

Textiles are wetted much more quickly with organic solvents than with water containing wetting agents. Also organic solvents give better penetration of textile fabrics and enable fabrics to be processed at higher speeds.

Other technical effects are based on the different swelling properties of textile fibres in organic solvents and in water. Furthermore, the solubility and reactivity of substances are not the same in solvents as in water. Solvent processing thus presents completely novel chemical and procedural characteristics. Ofcourse, in addition to its advantages, solvent processing is not without certain disadvantages. Brunscheiler has analysed the 'pros' and 'cons' and concludes that, despite many outstanding problems, solvent dyeing will go from strength to strength (153). The various aspects of solvent dyeing are reviewed by Milicevic (154) and Shipman (155).

The concept of solvent dyeing or in general solvent processing of textiles seems to be well accepted. Considerable interest has been shown in solvent dyeing of synthetic fibres with disperse dyes. However, very little information is available on the solvent dyeing of cellulosic fibres. This is mainly due to the fact that the dyes which are suitable for the dyeing of cellulosic fibres are insoluble in chlorinated solvents used on a commercial scale. Moreover, cellulosic fibres swell very little in such solvents. Therefore, the use of water or a suitable polar solvent at some stage is almost inevitable for the dye solubilization and fibre swelling.

Stevens and Peters made attempts to dye cotton and viscose with direct, acid and reactive dyes from solvents such as n-butanol, n-amyl alcohol, n-hexanol etc. (156,157) containing little amount of water. It was pointed out that the dye uptake was dependent on the presence of an optimum amount of water in the solvent systems. If this amount of water was decreased the dye uptake was uneven and was restricted only to the fibre surface and if it was increased the dye uptake was diminished. The dyeing of unswollen cotton with direct dyes from DMF and DMF-Perchloroethylene-Ethyleneglycolethylether solvent mixture is reported in a paper from the Delaware Valley Section of AATCC (158). An emulsion system containing dye, an emulsifying agent, water, glycerol and perchloroethylene is also reported by Siver for the dyeing of cellulosic fibres with direct and reactive dyes (159).

Morton has observed that unmercerised cotton absorbed direct dyes more rapidly from ethanol than mercerised cotton or viscose (160). Similar behaviour was noticed by Valko and Coworkers during the dyeing of unmercerised and mercerised cotton with Phenamine Brill. Violet B from absolute ethanol (161).

Suda and Nakajima studied the absorption of direct dyes on cellulosic fibre from aqueous alcoholic solutions (162). Recently the absorption of anionic dyes on water-swollen solvent-exchanged cotton from dimethyl formamide and trichloroethylene solvent mixture have been studied (163). Chavan has carried out solvent dyeing of cotton with reactive dye (164). This study is of importance because the hydrolysis of a reactive dye in aqueous system is almost inevitable. If the presence of water in the dyebatch is reduced or eliminated the dye hydrolysis could be minimized or avoided leading to higher dye fixation on cotton. Keeping this idea in view, in the present study some reactive dyes are applied on cotton from dimethylformamide-trichloro ethylene (DMF-TCE) solvent mixture by exhaustion method and to study the dyeing mechanism. The advantage of this solvent mixture is that the dyes used are soluble in DMF and their solubility could be desired with the addition of TCE. In order to open up the fibre structure and to get maximum dye exhaustion the pre-swelling of cotton with water was essential (165). The alkali to be used for dye fixation on fibre was also insoluble in solvent mixture. Hence it was incorporated in the fibre using aqueous alkaline solutions during pre-swelling treatment.

3:10:1 Cotton Dyeing

Although reactive dyes are often applied by pad-batch or continuous methods, exhaustion techniques are also quite useful. The dyes possess low affinity for cellulosic fibres, therefore addition of large quantities of electrolyte is often recommended as the dye fixation depends on how closely it is associated with the fibre. Any method which can produce better exhaustion is likely to yield better dye fixation on fibre. In case of reactive dyes better fixation would be obtained when greater portion of dye is closely associated with the fibre. Thus the conditions which are likely to give maximum exhaustion may also give higher dye fixation (166). Keeping this in view, the effect of DMF-TCE ratio, alkali concentration used for pre-swelling, temperature and time are studied in order to standardise the conditions to get optimum dye exhaustion and dye fixation. The results are given in Tables 40 to 43.

3:10:1:1 Effect of DMF-TCE Ratio

It can be seen from Table-40 that at suitable DMF-TCE ratio it is possible to get 100% exhaustion of all dyes. Ofcourse, this ratio is different for individual dyes. Generally 1:1 DMF : TCE ratio is found most suitable for 100% exhaustion, however, the dye DN-2 requires 1:0.5 DMF-TCE ratio for 100% exhaustion. When the TCE concentration was increased, i.e. at 1;2, 1:3 and 1:4 DMF-TCE ratios the % exhaustion remains unchanged. The maximum % fixation is observed in 1:1 to 1:2 DMF-TCE ratio. For various dyes it follows following order,

DN-2	DN-5	DN-7	DN-10
1:0.5	1:2	1:2	1:2

At higher levels of DMF-TCE ratio the dye fixation was decreased. The reason for such behaviour as given by Chavan, is complete dye precipitation in the dye bath resulting in poor dye penetration in the fibre, giving low dye fixation (167).

TABLE 40

Effect of DMF-TCE Ratio on Dye Exhaustion and Fixation

Dye No.	DMF-TCE Ratio				
	1:0.5	1:1	1:2	1:3	1:4
DN-2					
Exhaustion %	100	100	100	100	100
Fixation %	82.0	81.0	76.0	51.0	29.0
DN-5					
Exhaustion %	90	100	100	100	100
Fixation %	71.0	79.0	82.0	64.0	43.0
DN-7					
Exhaustion %	92	100	100	100	100
Fixation %	70.0	80.0	82.0	49.0	29.0
DN-10					
Exhaustion %	85	100	100	100	100
Fixation %	65.0	75.0	81.0	55.0	33.0

TABLE 41

Effect of Alkali Concentration on Dye Fixation

Alkali Concentration g/1	% Fixation			
	DN-2	DN-5	DN-7	DN-10
5	62	64	66	69
10	71	73	70	77
15	73	76	75	80
20	79	80	80	82
30	82	83	82	80
40	75	74	78	73
50	73	70	71	68

TABLE 42

Effect of Temperature on Dye Fixation

Temperature °C	% Fixation			
	DN-2	DN-5	DN-7	DN-10
50	68	70	72	74
60	73	73	76	77
70	78	79	80	82
80	82	82	83	82
90	84	84	85	85
100	84	85	85	86

TABLE 43

Effect of Time on Dye Fixation

Time Minutes	% Fixation			
	DN-2	DN-5	DN-7	DN-10
15	73	70	72	75
30	77	75	76	80
45	80	81	81	82
60	82	83	82	83
120	83	83	83	83
180	84	84	84	84

3:10:1:2 Effect of Alkali Concentration

The effect of alkali concentration in pre-swelling of cotton on dye fixation is shown in Table 41. The pre-swelling of the samples was carried out in aqueous sodium hydroxide over a range of 5-50 g/l concentration. Initially the increase in alkali concentration increases % dye fixation, but after 30 g/l concentration, decrease in fixation was observed, with the exception of dye DN-10, where 20 g/l concentration is the maximum dye fixation concentration. These results are comparable with the reported results for other types of dyes (168). The initial increase in dye fixation may be attributed to the fibre swelling and ionization (169), because even at 10 g/l alkali present on sample is sufficient to give complete dye fixation, as calculated from theoretical alkali consumption values. Beyond 30 g/l alkali concentration dye hydrolysis became more prominent, resulting in low dye fixation.

3:10:1:3 Effect of Temperature

To study the effect of temperature on dye fixation, at constant alkali concentration (20 g/l) and at different temperatures, dyeing was carried out. The results thus obtained are given in Table 42. The clear fact that reveals is the increase in temperature increases the dye fixation but beyond 80°C noticeable increase is not taking place.

3:10:1:4 Effect of Time

From Table 43, it appears that most of the dye fixation took place during 1 hr, although only a slight increase was observed when the fixation time was extended upto 3 hours.

From these tables (40-43) the optimum dyeing conditions can be 1:1 DMF-TCE ratio, 30 g/l pre-swelling alkali concentration, 80°C temperature and 1 hour dyeing period.

3:10:2 Alkali Estimation

After standardisation of optimum dyeing conditions, attempt was made to estimate alkali utilized during dyeing. One of the functions of alkali in reactive dyeing is to neutralise the HCl liberated during dye-fibre reaction and thus carrying the reaction in the forward reaction.

In order to know the exact amount of alkali consumed during dye-fibre reaction, the amount of alkali present on the fibre before dyeing, after treatment in blank dyebath and after dyeing was estimated at 20 g/l alkali concentration of pre-swelling. The results are presented in Table 44. The theoretical alkali consumption was calculated from the amount of dye fixed on fibre and the structural formula of each dye whereas, the experimental values of the alkali consumption were calculated from the difference between the alkali present on fibre after treatment in blank dyebath and after dyeing.

It is seen that part of alkali comes out from the fibre during the dyeing process itself as indicated by the reduction in alkali concentration after treatment in blank dyebath.

The results of the actual amount of dye consumed during dyeing showed that higher the amount of dye fixed on fibre higher was the alkali consumption during dyeing. This was in agreement with the theoretical alkali consumption. However, the values obtained from the experimental results are higher than those obtained from theoretical calculations.

3:10:3 Estimation of Dye Hydrolysis

At the end of dyeing, the total amount of dye present on fibre would be in the form of dye reacted with fibre, hydrolysed dye and unreacted dye which is still in the reactive form. The results of the quantitative analysis

TABLE 44

Alkali Consumption During Dyeing

DYE NO	Amount of Alkali on Sample g/0.2g			Alkali Consumption	
	Before Dyeing	After Blank Dyeing	After Dyeing	Experimen-tal	Theoretical
	$x10^{-3}$ a	$x10^{-3}$ b	$x10^{-3}$ c	$x10^{-3}$ b-c	$x10^{-3}$
DN-2	4.19	1.41	0.69	0.72	0.52
DN-5	4.19	1.41	0.76	0.65	0.48
DN-7	4.19	1.41	0.73	0.68	0.48
DN-10	4.19	1.41	0.72	0.69	0.44

of these three forms from the solvent mixture at 20 g/l alkali concentrations are shown in Table 45. From these results it becomes clear that dye hydrolysis also took place from DMF-TCE solvent mixture.

3:11 RATE OF HYDROLYSIS

The physico chemical analysis of the fibre-reactive dyeing is most simply considered in the first instance in terms of the hydrolysis reaction and in the second by taking into account a competing alcoholysis (or aminolysis) reaction in the same phase. The principles thus established may then be applied to the dyeing situation involving two phases (fibre and aqueous solvent). This approach provides a basis for the discussion of fixation.

The hydrolysis behaviour of reactive dyes has several important technical values:

(i) stored dye powders may decompose in the presence of atmospheric moisture;

(ii) Solutions and print pastes containing reactive dyes may deteriorate on standing;

(iii) Hydrolysis may compete excessively with the very similar dye fixation reactions, i.e. with OH, SH, or NH_2 groups.

TABLE 45

Estimation of Dye Hydrolysis on Fibre

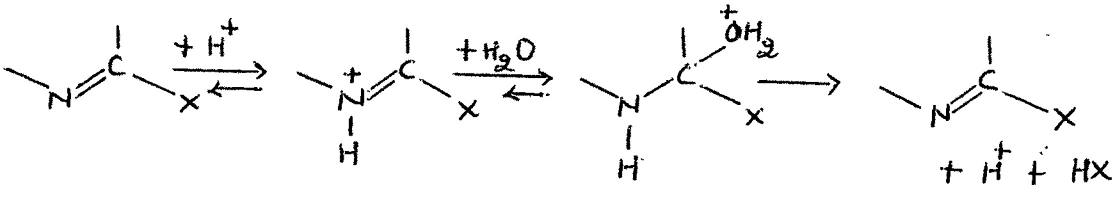
Dye No.	Dye Fixed %	Dye in reactive form %	Hydrolysed dye %
DN-2	79.5	18.0	2.5
DN-5	83.5	12.5	4.0
DN-7	81.0	15.5	3.5
DN-10	82.5	13.0	4.5

Thus the consideration of hydrolysis kinetics is of primary importance. The derivation and determination of the reactivity of a reactive dyestuff in an aqueous alkaline medium are based on the equation for bimolecular reactions which can be assumed as valid for most reactive systems. According to this equation, the decrease with time (-d (D)) of the reactive dyestuff concentration [D] of a dyestuff solution is proportional to the dyestuff concentration and the base concentration $[OH^-]$.

$$\frac{-d\ (D)}{dt} = K\ [OH^-]\ [D]_t \ \ldots\ldots \quad (i)$$

Where $[D]_t$ and $[OH^-]_t$ are the concentrations of dye and hydroxyl ions at time t.

Water is itself a very weak nucleophile, and the reaction rate with dyes of technical interest is very slow indeed. However, the reaction rates may be increased if the electrophilic nature of the active carbon atom is increased and this can occur when protonation of a nearby atom occur eg.



Thus the hydrolysis reaction may in appropriate cases be acid-catalysed, particularly when a proton accepting hetero atom is present in the reactive system, eg. dichloro triazinyl dyes. In the dry powders, these hydrolyze extremely slowly due to atmospheric water, but such hydrolysis leads to liberation of hydrochloric acid. This acid can act as an acid catalyst by protonation, leading to an increasingly autocatalyzed hydrolysis rate. However, the nucleophilic groups involved in dye fixation onto fibres are not sufficiently active under acidic conditions and therefore in majority of cases acid-catalysed fixation is not important. Thus apart from the important question of powder storage stability the main conditions of hydrolysis that have to be considered involve alkaline solutions.

It is clear from eq. (i) that in a buffered system in which $[OH^-]_t$ is a constant, then the second order rate constant K may be replaced by a pH dependent pseudo-first order rate constant K' as

$$\frac{-d(D)}{dt} = K\,[OH^-]_t \cdot [D]_t$$

$$= K'\,[D]_t \quad \ldots . \text{(ii)}$$

It can be seen that if K' is determined by appropriate standard means from experimental data, then since

$$K' = K \cdot [OH^-]_t$$

$$\log K' = pH + \log K.\bar{K} \qquad \ldots . \quad (iii)$$

$\bar{K}$ is the ionic product of water so the graph of pH → log K' should be straight line and slope should be unity. But extensive investigation of the hydrolysis kinetics of reactive dyes by number of researchers (37, 169-180) have shown that in majority of cases this simple relationship is not observed. Instead, five general kinds of relationship are observed, as illustrated in Fig.9.

Two main experimental methods are generally used for the study of hydrolysis in the case of reactive heterocyclic dyes containing chlorine as the leaving group. The first and most obvious one is to analyse the system for chloride ion released by hydrolysis using standard electrometric titration techniques. The second and very convinient method is spectroscopically. The optical density of the appropriate wavelength achieved is proportional to the amount of reactive dye present.

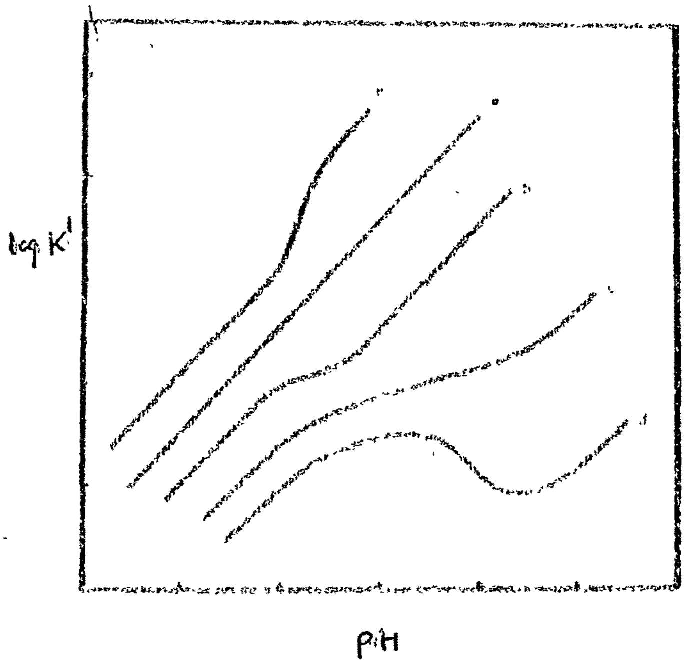
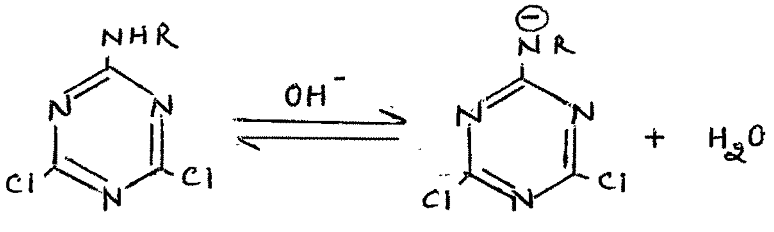


Fig. 9. General forms of log K^1 versus pH relationship observed with tri- and diazinyl reactive dyes.

In the present investigation for determining rate of hydrolysis of reactive naphthol, the first method was used. The pseudo-unimolecular rate constants obtained at various pH values are given in Table 46 and a plot pH log k' is shown in fig.10 .

Horrobin observed behaviour in accordance with curves b and c (fig 9), while studying the hydrolysis of model compounds and suggested that the cause lay in the loss of a proton by the imino bridging group to form a less reactive species. The reaction kinetics is analysed as follows:



I II

If the dye I is represented as D and II as D$^-$, then the stoichometric equations for the process is given as

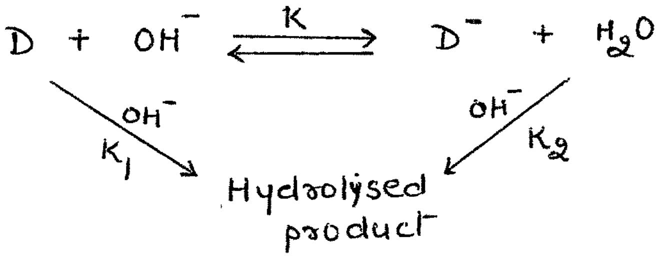


TABLE 46

Rate of Hydrolysis of Reactive Naphthol

pH	Rate constant K' $\times 10^3$ min^{-1}	log K'
7.9	0.158	-3.80
8.8	0.562	-3.25
9.5	1.78	-2.75
10.2	5.62	-2.25
11.0	19.90	-1.7
11.5	56.00	-1.25

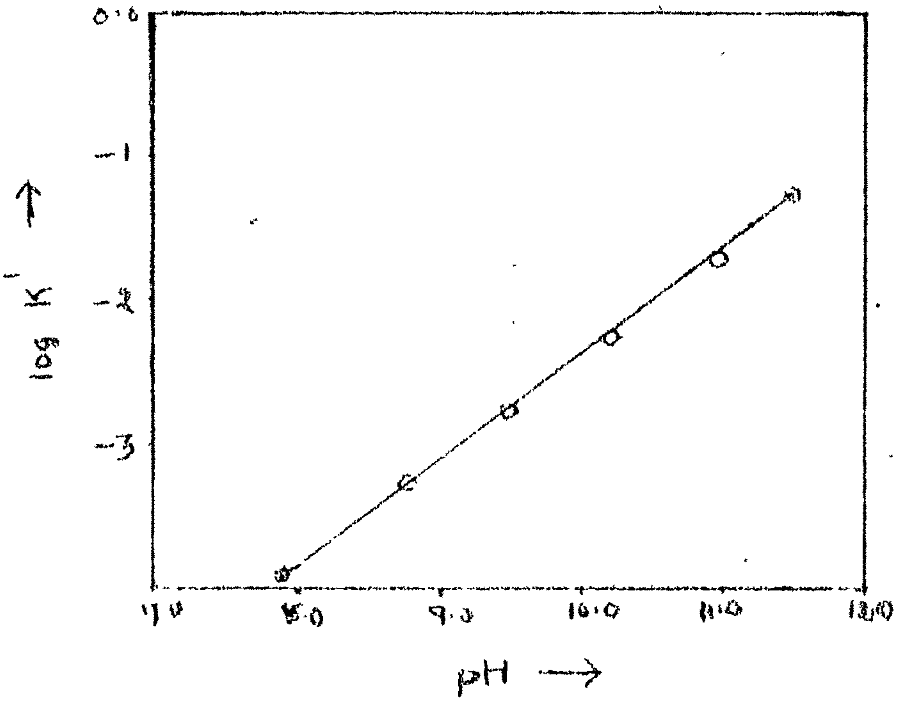


Fig. 10 Plot of log K^1 ⟶ pH for reactive naphthol

K_1 and K_2 are bimolecular hydrolysis constants for dyes D and D^-. Since the total dye present at any time is the sum of the quantities of D and D^-, then

$$[\bar{D}] = [D] + [D^-] \quad .. \quad (iv)$$

where $[\bar{D}]$ is the total dye concentration.

Now for acid base equilibrium

$$K = \frac{[D^-][H_2O]}{[D][OH^-]} \quad .... \quad (v)$$

Equations for $[D]$ and $[D^-]$ can be obtained in terms of $[\bar{D}]$ as

$$[D] = \frac{K'\,[\bar{D}]}{K' + [OH^-]} \quad ..... \quad (vi)$$

$$[D^-] = \frac{[\bar{D}]\cdot[OH^-]}{K' + [OH^-]} \quad ..... \quad (vii)$$

The observed hydrolysis rate is the rate of disapperance of the total reactive dye, which is given as

$$-\frac{d\,\bar{D}}{dt} = -\frac{dD}{dt} - \frac{d\,D^-}{dt}$$

$$= K_1\,[OH^-]_t\,[D]_t + K_2\,[OH^-]_t\,[D^-]_t$$

$$...... \quad (viii)$$

combining equations vi, vii & viii we get

$$-\frac{d\bar{D}}{dt} = \frac{K_1 [OH^-] K' \cdot [\bar{D}]_t}{K' + [OH^-]} + \frac{K_2 [OH^-]^2 \cdot [\bar{D}]_t}{K' + [OH^-]}$$

$$= [\bar{D}]_t \cdot [OH^-]_t \cdot \frac{K_1 K' + K_2 \cdot [OH^-]}{K' + [OH^-]} \quad \ldots \text{(ix)}$$

This equation shows that bimolecular or pseudo-first order kinetics will be observed according to whether OH^- is kept constant or not, and that when OH is kept constant the bimolecular rate constant is pH - dependent and equal to expression

$$\frac{K_1 K' + K_2 \cdot [OH^-]}{K' + [OH^-]} \quad \ldots . \quad \text{(x)}$$

At lower pH values, when $[D^-] \rightarrow 0$, the constant will equal to K_1, at higher pH values will tend toward K_2.

In the present investigation only straight line is observed - indicating pseudo - first order kinetics. Due to -C - C - bridging systems, the loss of proton is not possible and other form of reactive component is not possible.

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