CHAPTER - 3

USE OF HYDROXYANTHRACENE DERIVATIVES IN AZOIC DYEING OF COTTON

INTRODUCTION

INTRODUCTION

The insoluble azo dyes are formed on the fibre in two steps, by combination of a diazotized organic amine in solution with a naphthol, previously impregnated onto 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.

Read, Holliday and Sons discovered in 1880 that a fast red shade be produced with 2-naphthol coupled on the fibre with a solution of diazotized 2-naphthylamine. By 1890, Paranitroaniline Red (Para Red) became the vogue; this dye was produced by coupling 2-naphthol on the fibre with a solution containing diazotized p-nitroaniline and sodium acetate.

An important advance was made around 1912 when Chemische Fabrik Griesheim- Elektron introduced Naphthol AS, the anilide of 3-hydroxy-2-naphthoic acid as azoic coupling component. Not only was the new "ground" for insoluble azos found to have more affinity for cotton than 2-naphthol, but such dyeings were much faster, especially to sublimation, besides being faster than Para Red to light and rubbing.

The range of Naphthol AS compounds (azoic coupling components) and azoic diazo components increased rapidly.

The Colour Index(1) lists fifty-one of the former and sixty-two of the latter. Some of these are summarized in charts 1 and 2. With such a large selection of components it is possible to produce a very wide range of shades including yellows, oranges, scarlets, reds, maroons, violets, navy blues, greens, browns and blacks. The greatest utility in dyeing with Naphthols is in the deep shades of oranges, scarlets, reds, maroons, navy blues, browns and blacks.

A brief survey of the recent development in this field is discussed here. However, it has not been considered necessary to include a general review of the azoic dyes, because this subject has been dealt with in considerable details in many monographs(22-26) and in many text books(27-31).

Metallised Azoic Dyes:

In recent years metallisable azoic dyes have been manufactured by Farbwerke Hoechst. The Variogen Bases and Salts marketed by this firm can be applied with conventional Naphthols and after metallised with cobalt or copper salts to give green, gray or dark blue shades with outstanding fastness to rubbing, very good fastness to peroxide and excellent fastness to light(32-37). Brown shades are obtained by developing naphtholated cotton in a suitablly buffered

CHART 1.

Commercially Available Coupling Components

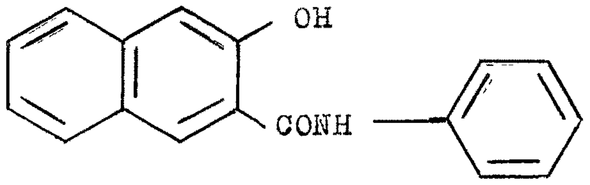
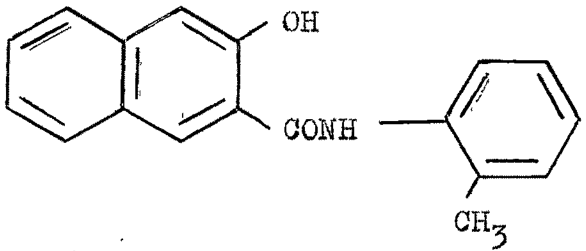
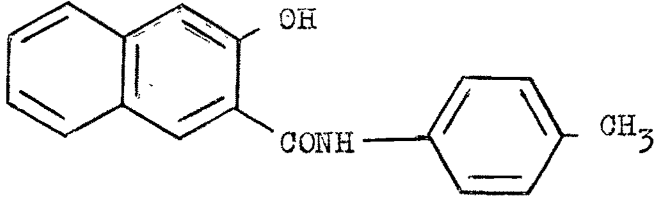
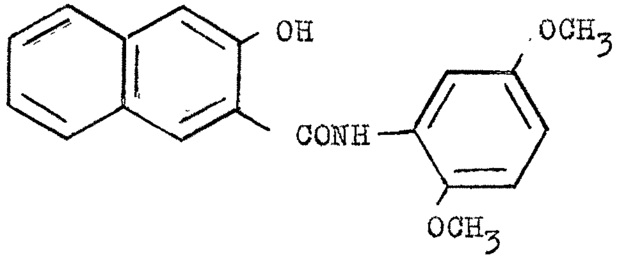
No 1.	Name 2.	Constitution 3.	Reference 4.
1.	Naphthol AS		2
2.	Naphthol AS-D		2,3
			4
3.	Naphthol AS-BG		2,5

Chart 1 (cont.)

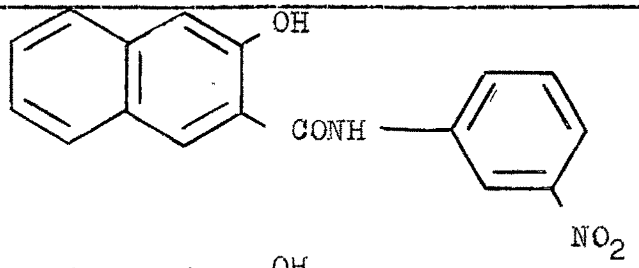
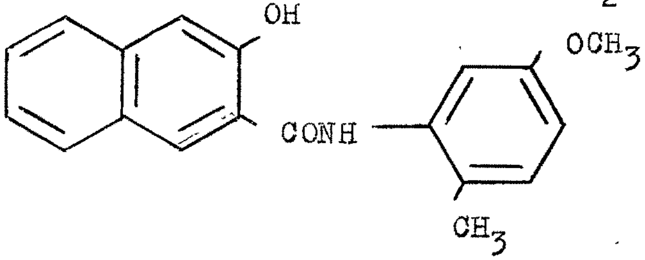
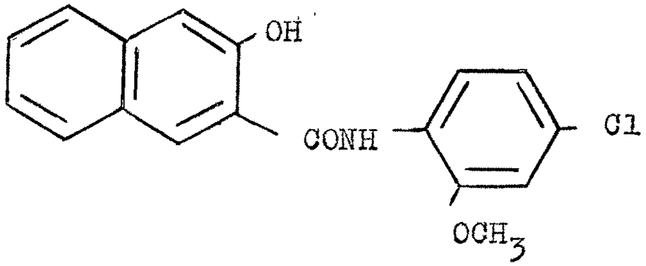
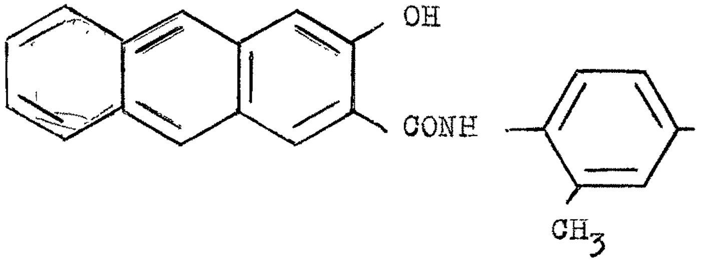
1.	2.	3.	4.
4.	Naphthol AS-BS		6,7
5.	Naphthol AS-RL		8
6.	Ciba naphthol RCA		9
7.	Naphthol AS-GR		10,12

Chart 1 (cont.)

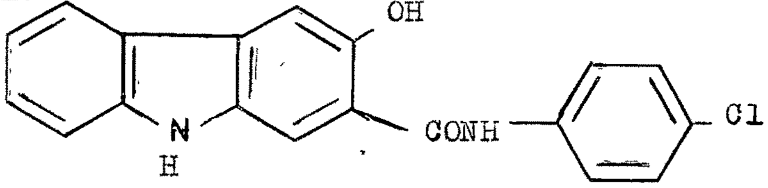
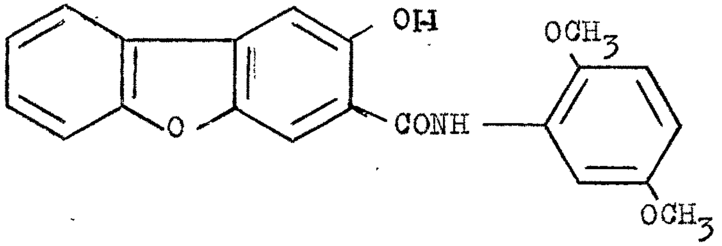
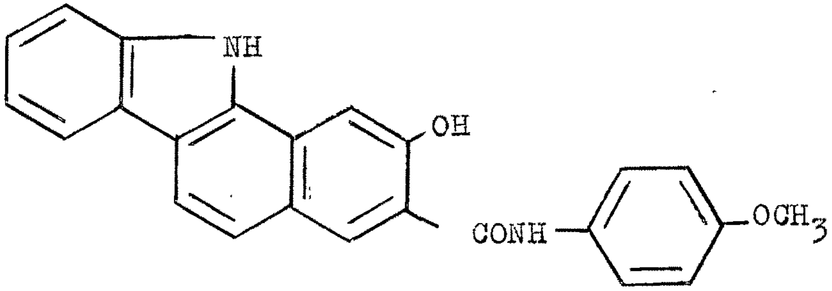
1.	2.	3.	4.
8.	Naphthol AS-IB		10,11,13
9.	Naphthol AS-BT		14
10.	Naphthol AS-SG		10,11,14

CHART - 2

Azoic Diazo Components

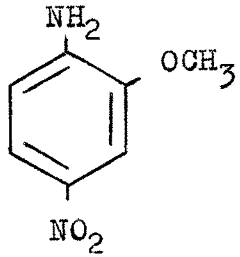
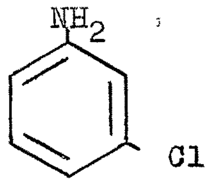
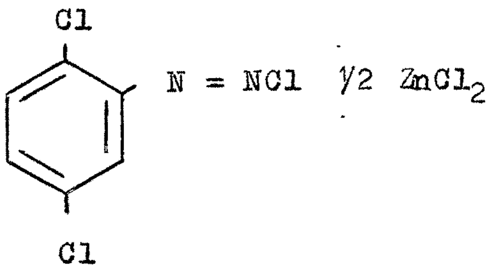
No. 1.	Name 2.	Constitution 3.	Reference 4.
1.	Fast Red B Base		6
2.	Fast Orange GC Base		15
3.	Fast Scarlet GG Salt		16

Chart 2 (cont.)

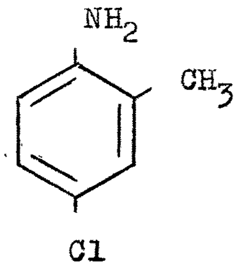
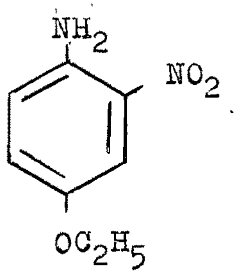
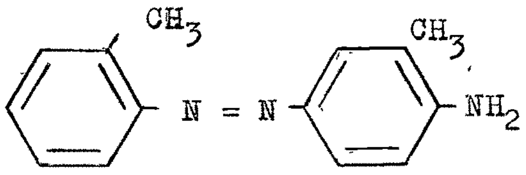
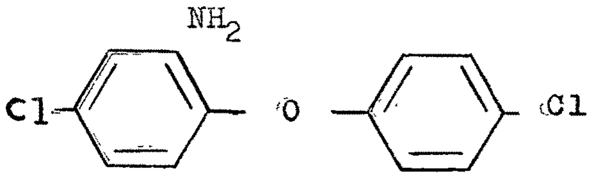
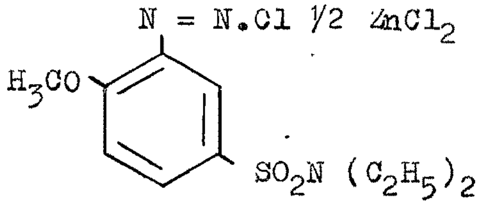
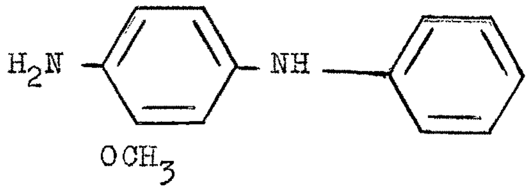
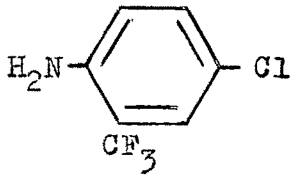
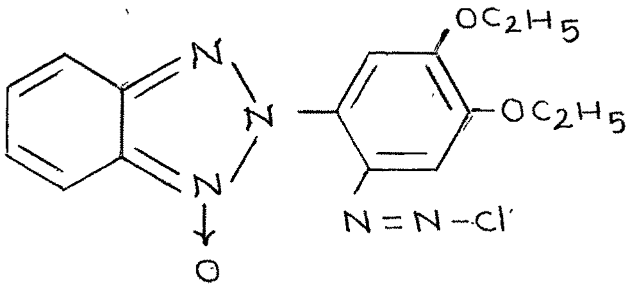
1.	2.	3.	4.
4.	Fast Red TR Base		17
5.	Fast Blue Red O Base		18
6.	Fast Garnet GBC Base		6
7.	Fast Red FR Base		4,19

Chart 2 (cont.)

1.	22.	3.	4.
8.	Fast Red ITR Base		10
9.	Variamine Blue FG		20
10.	Fast Scarlet VD Base		21

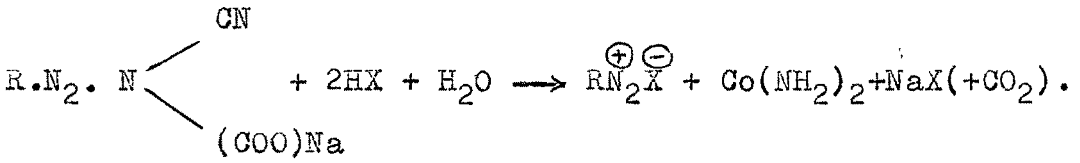
bath containing a diazotized aminoarylbenzotriazole oxide(I) such as :



and after treating with a salt of copper, cobalt or nickel(38). The use of 8-aminoquinoline and its derivatives as Fast Bases, after metallised with copper, cobalt or nickel salts give predominently brown shades with azoic coupling components(39).

<u>Azanil Salts</u> :

A short range of Azanil colour salts has been introduced by Farbwerke Hoechst. These are water soluble diazoamino compounds intended for application to cellulosic fibres from dyebaths which also contain a highly substantive member of the Naphthol AS series. When the components have been adsorbed by the fibre, dye formation is brought about by acidification of the dyebath. The structures of the azanil salts are corresponding to that obtained by coupling diazotized arylamines or tetrazotised diamines with a compound such as sodium cyanamide or cyanamidecarbozylate(40,41). According to the inventors active diazonium salts are regenerated by a reaction with aqueous acid (HX) which may be represented as follows :



$$R.N_2.N\begin{matrix}CN\\(COO)Na\end{matrix} + 2HX + H_2O \longrightarrow R\overset{\oplus}{N_2}\overset{\ominus}{X} + Co(NH_2)_2 + NaX(+CO_2).$$

In contrast with the liberation of diazonium salts from conventional diazoamino compounds this reaction is not reversible.

<u>Reactive Naphthols</u> :

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 precautions- such as :

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

(b). adding proper dispersi~~ve~~ng agents in the developing bath and

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

Even though 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 binding the naphthol covalently on the fibre, so that naphtholate foundation can be treated with hot soap solution before development, thus making the azo pigment in the developer bath, with a weak binding. The colours developed in this manner possess 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 bound naphthol before the coupling. In literature a number of patents are available describing the use of reactive naphthols(42-45). Broecker et. al. have synthesized reactive naphthols and have tested them as reactive azoic coupling components(46). Recently Shah and Upasani have reported the use of reactive naphthol and reactive anthracenol in azoic dyeing of cotton and wool(47,48).

Present Work :

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, attempts have been made to utilize hydroxyanthracene derivatives. Azo derivatives of 1-hydroxyanthracene have been reported (49-52). Since long back BON acid analogue of anthracene has been claimed as azoic coupling component(53). Use of 9-hydroxyanthracene as a coupling component is also reported(54). Recently some more azo derivatives of 9-hydroxyanthracene have been prepared and studied(55,56). It is therefore thought of interest to study the hydroxyanthracene derivatives in azoic dyeing of cotton.

The following seven derivatives of hydroxyanthracene were synthesized by the known methods and have been studied as azoic coupling components :

(i) 1-Hydroxyanthracene
(ii) 2-Hydroxyanthracene
(iii) 4-Acetyl-1-hydroxyanthracene
(iv) 1-Acetyl-2-hydroxyanthracene

(v) 1-Hydroxyanthracene-2-carboxylic acid

(vi) 1,5-Dihydroxyanthracene and

(vii) 1,8-Dihydroxyanthracene.

The dyed materials have been evaluated for their fastness properties.

EXPERIMENTAL

EXPERIMENTAL

Synthesis of Hydroxy Anthracene Derivatives :

(i) Preparation of 1-hydroxyanthracene :

Potassium salt of anthracene-1-sulphonic acid was prepared by sulphonation of anthraquinone in presence of yellow mercuric oxide. This was converted into the potassium salt of anthracene-1-sulphonic acid by reduction with zinc dust and liquor ammonia (sp.gr. 0.92) according to Schmidt(57).

The potassium salt of anthracene-1-sulphonic acid on fusion with alkali according to Dienel(58) gave 1-hydroxyanthracene as follows :

Potassium hydroxide (35g) was taken in a nickel crucible and heated in a muffle furnace to about 200°C. Potassium salt of anthracene-1-sulphonic acid (10g) was added to the molten alkali in small portions with stirring and the temperature was then raised and maintained at 260°C for 3 hours. The melt after cooling was dissolved in ice cold distilled water (300 ml) and filtered. The filtrate was acidified and the precipitated solid was filtered, washed with water and dried. It was then dissolved in glacial acetic acid (200 ml) in cold, and filtered. The clear filtrate was added to hot water (1000 ml) and allowed to cool. 1-Hydroxyanthracene which was separated in the form of light brown shining needles, m.p. 152°C. Yield 5g. Dienel reported m.p. 150-153°C.

(ii) Preparation of 2-Hydroxyanthracene :

2-Hydroxyanthracene was prepared from 2-aminoanthraquinone by diazotisation and boiling with water by the method of Perkin(59). 2-Hydroxyanthracene was then prepared by reducing 2-hydroxyanthraquinone with aluminium amalgam in aqueous alcoholic ammonia according to Perkin and Hall(60).

To a boiling solution of 2-hydroxyanthraquinone (5g), liquor ammonia (50 ml), water (200 ml), alcohol (20 ml) and freshly prepared aluminium amalgam (from 4g of aluminium foil) was added, in portions, during twenty minutes. The heating of the mixture was continued for a further one hour. The reaction mixture was then filtered and the residue extracted with boiling ethyl alcohol (150ml). Hot water (100ml) was added to the boiling ethyl alcohol extract. The solution was cooled and kept in a refrigerator. 2-Hydroxyanthracene separated in brownish needles. It soften at 236°C. and melted at 248°C. Yield 2.0g. Perkin and Hall reported m. p. 248°C.

(iii) 4-Acetyl-1-Hydroxyanthracene :

1-Hydroxyanthracene on acetylation with acetic anhydride in presence of pyridine affords a product 1-hydroxyanthracne acetate(58), which on Fries migration gives 4-acetyl-1-hydroxyanthracene.

A solution of 1-hydroxyanthracene acetate(58) (1.2g) in nitrobenzene (20ml) was mixed with a solution of anhydrous aluminium chloride (1.3g; [illegible]) in nitrobenzene (10 ml), and the reaction mixture protected from moisture, was left for 48 hours at room temperature. It was then treated with ice and hydrochloric acid and the nitrobenzene was steam distilled. The black product obtained was repeatedly extracted with cold dilute alkali. The product obtained on acidification of the combined alkaline extract was dissolved in hot alcohol. On cooling, a small crop of crystals of 2-acetyl-1-hydroxyanthracene separated. The mother liquor on dilution with water gave 4-acetyl-1-hydroxyanthracne, which was crystallized from alcohol in yellow shining plates m.p. 260°C. Lele, Shah and Sethna report m.p. 260°C(61).

(iv) Preparation of 1-Acetyl-2-Hydroxyanthracne :

2-Hydroxyanthracene on acetylation yields 2-hydroxyanthracene acetate(62) which on Fries migration produces 1-acetyl-2-hydroxyanthracene.

A solution of 2-hydroxyanthracene acetate(62) (1.2g) in nitrobenzene (25ml) was mixed with a solution of anhydrous aluminium chloride (1.3g; [illegible]) in nitrobenzene (20 ml) and the reaction mixture, protected from moisture, was left for 24 hours at room temperature. It was then treated with ice and hydrochloric acid and the nitrobenzene was steam distilled. The residue was then taken up in ether and the etherial layer was repeatedly extracted with alkali. The product obtained on acidification of the alkaline extracts, crystallized from dilute alcohol in yellow needles m.p. 112°C, Shah and Sethna report m.p. 112°C(63).

(v) <u>Preparation of 1-Hydroxyanthracene-2-Carboxylic Acid</u> :

1-Hydroxyanthracene-2-carboxylic acid was prepared by heating 1-hydroxyanthracene with potassium bicarbonate at 120°C by the method of Laska and Haller(64) as follows:

1-Hydroxyanthracene (1 g) was thoroughly mixed with potassium bicarbonate (1.8g) and the mixture added to anhydrous glycerine (5 ml). The reaction mixture was heated at 120°C in an oil bath for 4 hours. Carbon dioxide was bubbled through the solution during heating. The reaction mixture was then treated with water and the solution was filtered. The product on acidification of the filtrate, crystallized from dilute alcohol, m.p. 200°C(d), reported m.p. 200°C(d).

(vi) and (vii). Preparation of (vi) 1,5-Dihydroxy-ANTHRACENE AND (vii) 1,8-Dihydroxyanthracene :

These two derivatives (vi) and (vii) of anthracene were prepared according to the method of Lampe(65) as described earlier in the chapter II.

Azoic dyeing of Cotton:

The dyeing was carried out as follows :

The coupling component (0.1g) was dissolved at room temperature in aqueous sodium hydroxide solution (10% 5ml) in a dye pot and the volume of solution was made to 100 ml with demineralized water. The cotton hank (5g) was wetted with water and after squeezing was impregnated in the solution and kept for 30 minutes at room temperature. The dye pot was placed in a water bath for further 30 minutes at 60-70°C. For more exhaustion of the hydroxyanthracene derivative 10% aqueous sodium chloride solution (20 ml) was added in small portions during the dyeing. The hank was squeezed and then developed in 3% neutral solution of diazotized amines. The different amines used for developing purpose are listed in Tables 1 to 7. The dyed hank was rinsed with cold water followed by boiling with 1% soap solution for half an hour. Again it was rinsed with cold water and dried. The shades obtained are recorded in Tables 1 to 7.

Colour Fastness to Washing :

Washing fastness of the dyed samples have been determined on Launder-Ometer according to AATCC IA test method(66) by staining. The test samples for washing fastness were prepared by interweaving the hank of dyed test sample (5g) with a hank of undyed sample (2.5g).

Launder-Ometer was adjusted to 40°C and wash liquor was prepared by dissolving 1 gram lux soap chips in 200 ml water in a stainless steel cylinder. After adding 10 stainless steel balls to each container the cover was clamped. The containers were then fastened in the addapters on the rotor of the Launder-Ometer with the covers facing the operator in such a manner that when the containers rotate, the cover strikes the water first.

The rotor was then started for two minutes to preheat the containers. It was then stopped and the cover of one container was unclamped and a well crumpled test specimen was entered into the solution and the cover was replaced and kept it without clamping. This operation was repeated until all the containers in the row had been loaded. Then covers were clamped. The Launder-Ometer was then run at 42 rpm for 45 minutes. After 45 minutes it was stopped and containers were removed and ~~made them~~ emptied empty.

Each specimen was rinsed twice in beakers in fresh 100 ml baths of water at 40°C for one minute period with occassional hand s~~e~~queezing. It was then scoured in 100 ml of a solution of acetic acid (0.05 ml of 28% acetic acid in 100 ml of water) for one minute at 27°C. It was again rinsed with 100 ml of water at 27°C, excess of moisture was then removed by Wringer rolls. The specimens were then dried and compared with gray scale for their washing fastness and are listed in Tables 1 to 7.

<u>Colour Fastness to Light</u> :

Light fastness of the dyed samples have been determined on ATLAS-FADE-OMETER according to AATCC test method(67) by making pads of the dyed fibres with the longer dimension lengthwise of the fibres and mounted them on white cardboard~~s~~ alongwith the standard samples and then on the holders supplied with the apparatus. The filled specimen holders were then placed on the specimen rack of the apparatus in proper vertical alignment. Fade-Ometer was then started and operated ~~it~~ with the light on until the test was completed. The temperature was adjusted to 60°C and the relative humidity of the air in the test chamber passing over the specimens was that produced by room air passing over wicks saturated by water.

Test specimens and standards were examined after exposure for period of 20 hours where "just appreciable fading" was observed. The results obtained by evaluating the test specimens with gray scale are given in Tables 1 to 7.

Fastness to Crocking :

Crocking fastness of the dyed samples have been determined on Crock-Meter of ATLAS ELECTRIC DEVICES CO. MODEL-1 according to AATCC test method by Dry crocking test(68).

Dyed yarn were wound on a card board of the size 5.1 x 12.7 cm with the yarn running in long direction and it was placed on the base of the Crock-Meter so that it rested flat with its long dimension in the direction of rubbing. Square of white testing cloth (lawn) 5.1 x 5.1 cm with the weave oblique to the direction of rubbing, over the end of the finger (1.5 cm dia.) which was projected downwards from the weighed sliding arm was mounted using special spiral wire clip.

Covered finger was then lowered on to the test specimen and caused ~~it~~ to slide back and forth twenty times by making ten complete turns of the crank at the rate of one turn per second. The White test square was then removed and (evaluated) the amount of colour transfered from the specimen to the white test square ~~under-examination~~ by means of grey scale for staining with intermediate steps.

Table 1

1-Hydroxyantharcene as a coupling component base, shade on the fibre and fastness properties :

No.	Base	Shade on the fibre	Washing fastness	Light fastness	Crocking fastness
1.	2.	3.	4.	5.	6.
1.	o-Nitroaniline	Reddish brown	4	3	2
2.	m-Nitroaniline	Brown	4	3	2
3.	o-Chloroaniline	Light scarlet	3-4	3	2
4.	m-Chloroaniline	Brown	4	3	2
5.	p-Chloroaniline	Brown	3-4	3	2
6.	2,3-Dichloroaniline	Brown	4	3	2
7.	2,4-Dichloroaniline	Brown	5	3	2

Table 1 (cont.)

1.	2.	3.	4.	5.	6.
8.	2,5-Dichloroaniline	Light scarlet	5	3	2
9.	2,6-Dichloroaniline	Light scarlet	5	3	2
10.	Benzidine	Khakhi	2	2	1
11.	o-Toluidine	Brown	3	2	2
12.	p-Toluidine	Light purple	2	3	2
13.	p-Anisidine	Brown	3	2	2
14.	p-Phenylenediamine	Brown	4	3	2-3

Table 2

2-Hydroxyanthracene as a coupling component. Base, shade on the fibre and fastness properties :

No.	Name of base	Shade on the fibre	Washing fastness	Light fastness	Crocking fastness
1.	2.	3.	4.	5.	6.
1.	o-Nitroaniline	Light orange	4	3	3
2.	p-Nitroaniline	Light orange	4	3	3
3.	o-Chloroaniline	Light orange	4	3	2
4.	m-Chloroaniline	Pink	4	3	2
5.	p-Chloroaniline	Pink	4	3	2
6.	2,3-Dichloroaniline	Orange	4-5	3	2
7.	2,4-Dichloroaniline	Light orange	4	3	3-4

Table 2 (cont.)

1.	2.	3.	4.	5.	6.
8.	2,5-Dichloroaniline	Pink	4	3	2-3
9.	2,6-Dichloroaniline	Orange	4	2	2-3
10.	Benzidine	Light violet	3-4	3	2-3
11.	o-Toluidine	Orange	3-4	3	3
12.	p-Toluidine	Light purple	4	3	3
13.	p-Anisidine	Pink	4	3	3
14.	p-Phenylenediamine	Light violet	3	3	2

Table 3

4-Acetyl-1-hydroxyanthracene as a coupling component. Base, shade on the fibre and fastness properties :

No. 1.	Name of base 2.	Shade on the fibre 3.	Washing fastness 4.	Light fastness 5.	Crocking fastness 6.
1.	m-Chloroaniline	Light pink	2	4	2
2.	p-Chloroaniline	Light pink	3	6	2
3.	5-Chloro-o-toluidine	Light pink	3	6	2
4.	4-Nitro-o-anisidine	Light pink	4	4	2
5.	3-Nitro-p-anisidine	Light pink	1	3	1-2
6.	3-Nitro-p-toluidine	Light pink	3	4	2
7.	4-Nitro-o-toluidine	Light pink	2	2	1

Table 3 (cont.)

1.	2.	3.	4.	5.	6.
8.	Dianisidine	Gray	3	6	2
9.	6-Benzamido-4-methoxy-m-toluidine	Light violet	3	4	2
10.	4-(o-Ethoxy)-benzeneazo-1-naphthylamine	Grey	2	4	1

Table 4

1-Acetyl-2-hydroxyanthracene as a coupling component. Base, shade on the fibre and fastness properties :

No. 1.	Base 2.	Shade on the fibre 3.	Washing fastness 4.	Light fastness 5.	Crocking fastness 6.
1.	m-Chloroaniline	Light pink	4	6	1
2.	p-Chloroaniline	Light pink	4	4	3
3.	5-Chloro-o-toluidine	Light pink	4	4	3
4.	4-Nitro-o-anisidine	Light pink	3	4	2
5.	3-Nitro-p-anisidine	Light pink	3-4	3-4	3

Table 4 (cont.)

1.	2.	3.	4.	5.	6.
6.	3-Nitro-p-toluidine	Light pink	3	4	1
7.	4-Nitro-o-toluidine	Light pink	3	3-4	1
8.	Dianisidine	Grey	3	4	1
9.	6-Benzamido-4-methoxy-m-toluidine	Light violet	3	4	2
10.	4-(o-Ethoxy)-benzeneazo-1-naphthylamine	Brown	3	3-4	1

Table 5

1-Hydroxyanthracene-2-carboxylic acid as a coupling component. Base, Shade on the fibre and fastness properties :

No.	Base	Shade on the fibre	Washing fastness	Light fastness	Crocking fastness
1.	2.	3.	4.	5.	6.
1.	o-Nitroaniline	Brownish orange	5	3	2
2.	m-Nitroaniline	Brownish orange	5	3	2
3.	p-Nitroaniline	Brownish orange	5	3	1-2
4.	o-Chloroaniline	Brownish orange	5	3	2
5.	m-Chloroaniline	Brownish orange	4-5	3	2
6.	p-Chloroaniline	Brownish orange	4	3	2
7.	2,3-Dichloroaniline	Brownish orange	4	3	2

Table 5 (cont.)

1.	2.	3.	4.	5.	6.
8.	2,4-Dichloroaniline	Brownish orange	3	3	2
9.	2,5-Dichloroaniline	Brownish orange	3	3	2
10.	2,6-Dichloroaniline	Brownish orange	3	3	2
11.	Benzidine	Khakhi	3	2	2
12.	o-Toluidine	Brown	4	3	2
13.	p-Toluidine	Reddish brown	4	3	2
14.	p-Aisidine	Light grey	2	3	1-2
15.	p-Phenylenediamine	Brown	2	2	1-2

Table 6

1,5-Dihydroxyanthracene as a coupling component. Base, shade on the fibre and fastness properties :

No.	Base	Shade on the fibre	Washing fastness	Light fastness	Crocking fastness
1.	2.	3.	4.	5.	6.
1.	o-Chloroaniline	Reddish brown	3	1-2	2
2.	m-Chloroaniline	Violet	4-5	4-5	2
3.	p-Chloroaniline	Violet	4-5	4-5	2-3
4.	p-Anisidine	Brown	3-4	5	2
5.	p-Toluidine	Yellowish brown	2	3	2
6.	Benzidine	Violet	3-4	3-4	2

Table 6 (cont.)

1.	2.	3.	4.	5.	6.
7.	o-Nitroaniline	Red	4	4	2
8.	3-Nitro-p-anisidine	Light violet	4	3	2
9.	3-Nitro-p-toluidine	Light violet	3	2	1
10.	4-Nitro-o-toluidine	Red	3-4	3	2
11.	5-Chloro-o-toluidine	Reddish brown	3	4	1-2
12.	Dianisidine	Grey	3	4	2

Table 7

1,8-Dihydroxyanthracene as a coupling component. Base, shade on the fibre and fastness properties :

No.	Base	Shade on the fibre	Washing fastness	Light fastness	Crocking fastness
1.	2.	3.	4.	5.	6.
1.	o-Chloroaniline	Reddish brown	2	3	1
2.	m-Chloroaniline	Reddish violet	4	5	2
3.	p-Chloroaniline	Reddish violet	4	5	2
4.	p-Anisidine	Brown	3	4	2
5.	p-Toluidine	Yellowish brown	3	3-4	2
6.	Benzidine	Violet	3-4	3-4	2

Table 7 (cont.)

1	2	3	4	5	6
7.	o-Nitroaniline	Red	4	5	2
8.	3-Nitro-p-anisidine	Light violet	3-4	3-4	1
9.	3-Nitro-p-toluidine	Light violet	3	3	2
10.	4-Nitro-o-toluidine	Red	3-4	3	1
11.	5-Chloro-o-toluidine	Reddish brown	2	2	1
12.	Dianisidine	Grey	3-4	2	2

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Azoic Shades :

The available naphthols are divided into two broad classes on the bases 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 all the hydroxyanthracene derivatives come in the second class. The 1-hydroxyanthracene gives brown shades with different bases, while 2-hydroxyanthracene gives orange type shades. 4-Acetyl-1-hydroxyanthracene and 1-acetyl-2-hydroxyanthracene produces light pink shades on the fibres. The brownish orange shades are obtained when 1-hydroxyanthracene 2-carboxylic acid is used as a coupling component. The 1,5 and 1,8-dihydroxyanthracene derivatives are giving reddish brown to reddish violet shades. Of course, in all cases, when base of high molecular weight is used for the development purpose, some higher shade is obtained. Thus a wide range of bright colour shades are obtained on application of these derivatives. The results are tabulated in Tables 1 to 7.

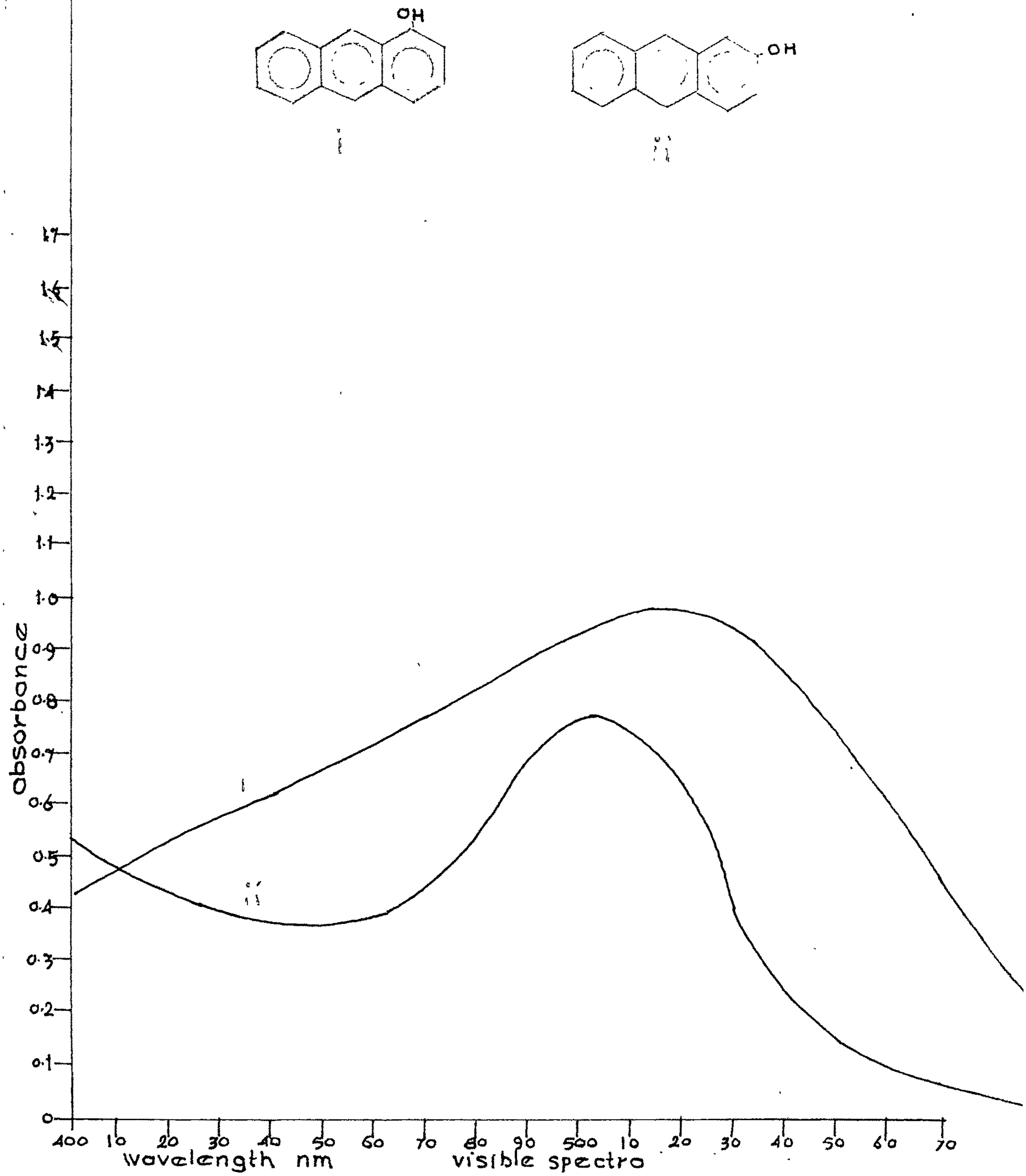
Comparision of shades of (i) and (ii) show that the former gives heavier shades than the later. (Tables 1 and 2). This behaviour was further studied by extracting the azoically dyed fibres with chloroform and subjecting the extract for absorption spectra. The absorption spectra (base used was p-cl-aniline) were taken on SPEKOL Spectrophotometer with 10 mm cell and are shown in figure 1. The (i) shows the absorption maxima at 515 nm, while (ii) shows the absorption maxima at 500 nm. The same behaviour has been observed by J. Morgenstern et. al.(69). They have reported that 1-hydroxy-2-(phenylazo)-anthracene shows absorption at greater wavelength than 2-hydroxy-1-(phenylazo)-anthracene.

Introduction of acetyl group in 1- and 2-hydroxy-anthracene gives interesting results (Table 3 and 4). Contrary to expectation, both the derivatives, (iii) and (iv), give~~s~~ lighter and ~~of a~~ reddish tinge shades. The effect due to the position occupied by the acetyl and hydroxyl group on the colour of the fibre is not observed remarkably. This can be again seen by comparing the absorption spectra of chloroform extract of dyed fibre (base p-cl-aniline) figure 2. The spectra shows that compound (iii) gives maxima at 470 nm while that of (iv) gives at 460nm. However, in case of the highly substituted bases (8,9 and 10); (iii) gives higher shades than (iv).

No substantial change in the shade is observed when the carboxyl group is introduced into the ortho position of the hydroxyl group (Table 5). The absorption spectra of chloroform extract of dyed fibre (base p-cl-aniline) shows maxima at 495 nm (figure 3).

At the stage of development, the diazonium group attacks a position which has been activated as a site of high electron density. Coupling therefore, takes place in ortho or para position to the directing hydroxyl group, but the mesomeric effect in the phenoxide ion tends to couple at the terminal carbon atom in a conjugated series of double bonds and gives the para substituted compounds(70). Because of this, dihydroxy aromatics are compounds which can give dual coupling on treatment with diazonium solution. With a hope to get higher shades in azoic dyeing the 1,5 and 1,8-dihydroxyanthracene have been tested as azoic coupling components. The results are encouraging. These two derivatives are giving higher shades than 1-hydroxyanthracene. The absorption spectra of chloroform extract of the dyed material (base p-chloroaniline) shows maxima at 540 and 530 nm for (vi) and (vii) respectively.(Fig.4).

Fig.no 8


OH
i
OH
ii
absorbance
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
10
20
30
40
50
60
70
80
90
500
10
20
30
40
50
60
70
i
ii
wavelength nm
visible spectra

2-Acetyl-1-Hydroxyanthracene
1-Acetyl-2 Hydroxyanthracene.

fig.no. 2

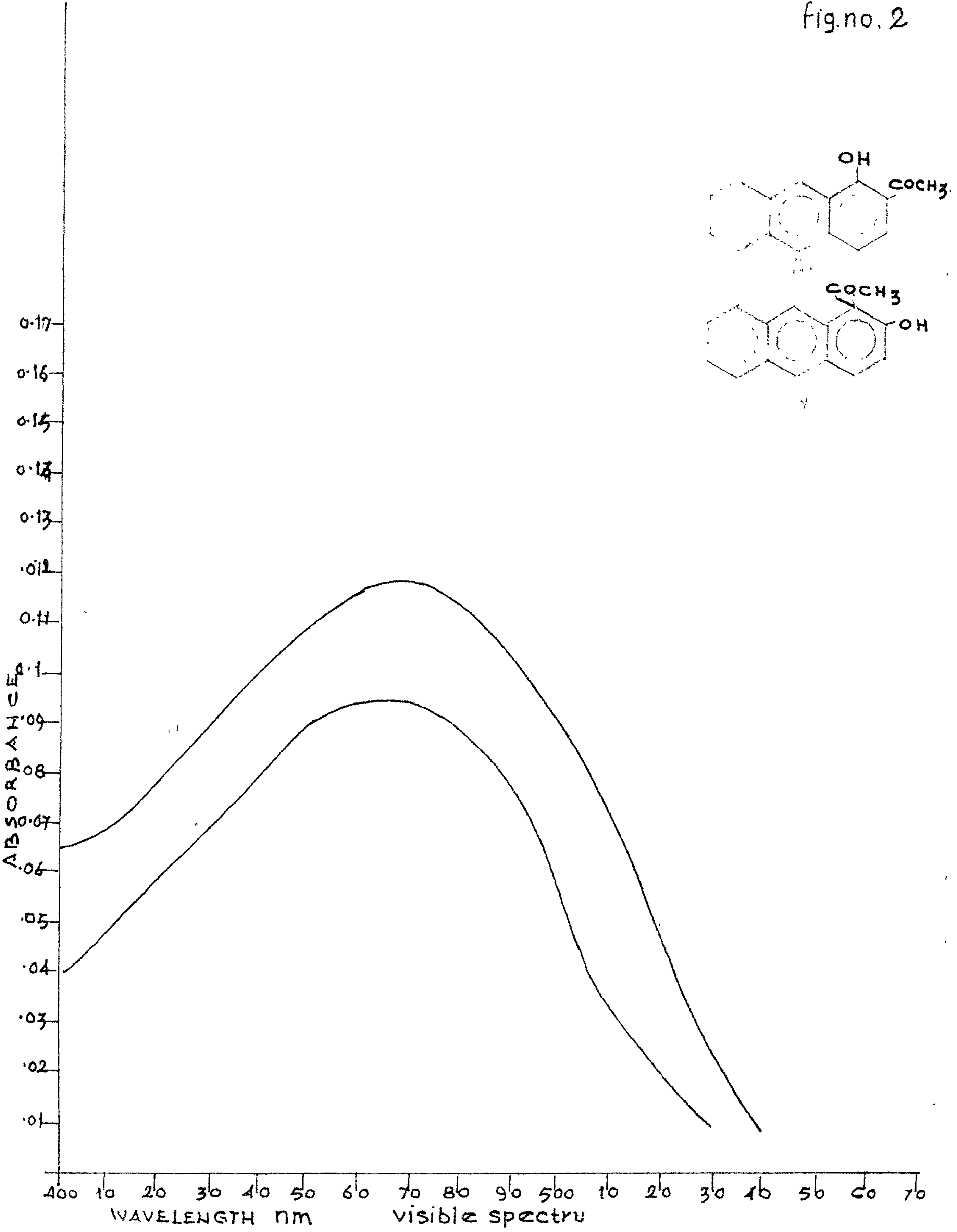


Fig.no.-3

1-Hydroxyanthracene 2-Carboxylic Acid.

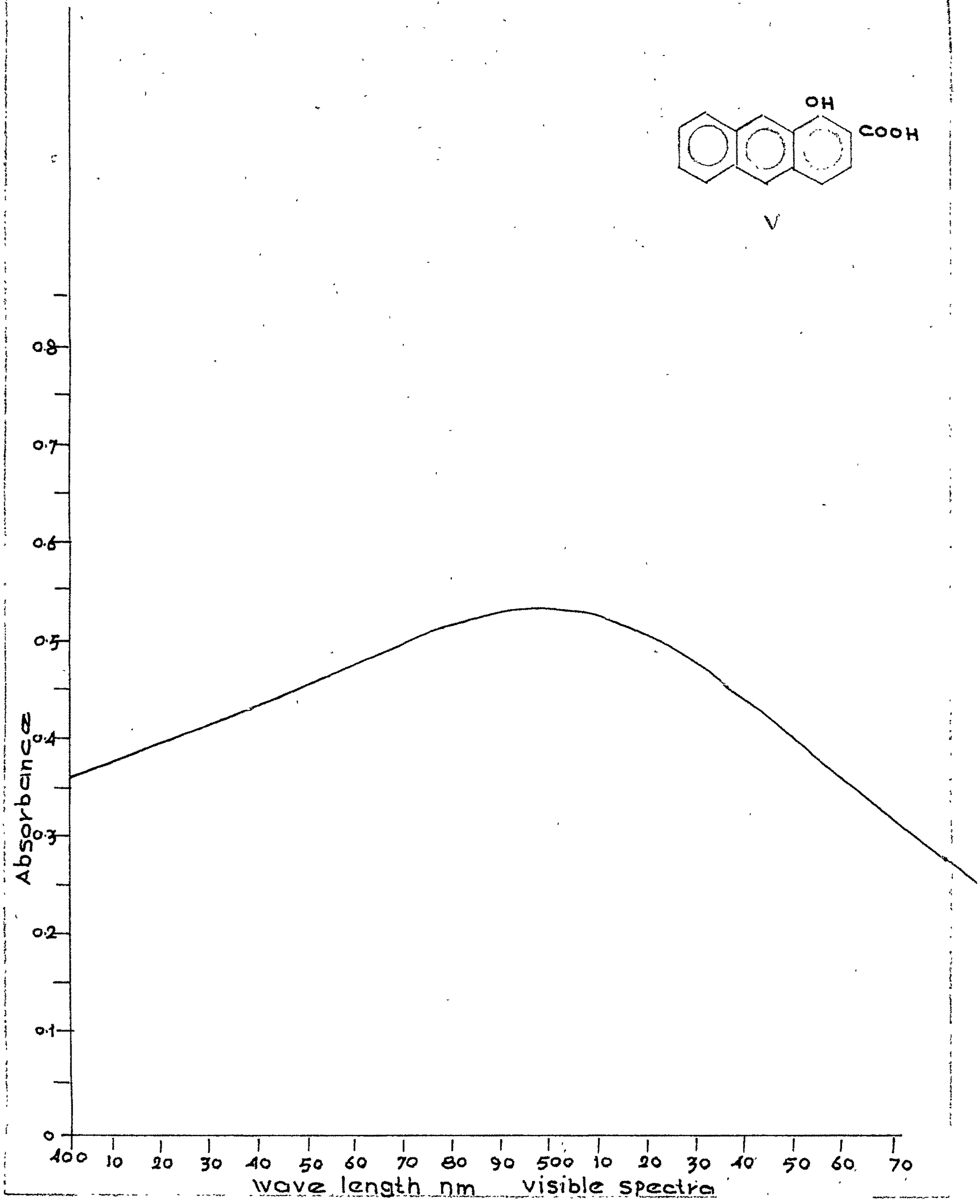
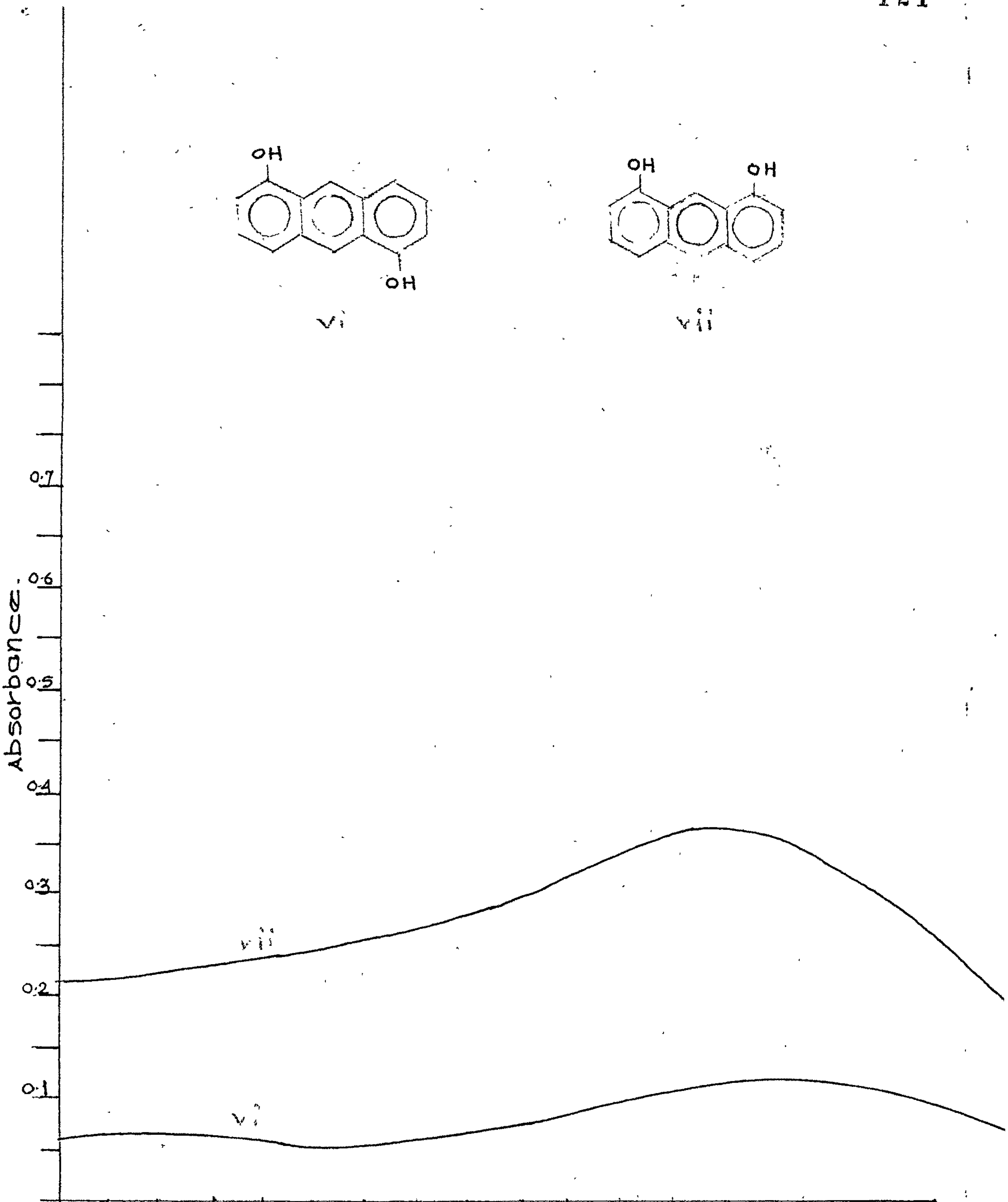


Fig.no. 4


OH
OH
vi
OH
OH
vii
Absorbance.
0·7
0·6
0·5
0·4
0·3
0·2
0·1
vii
vi
400
10
20
30
40
50
60
70
80
90
500
10
20
30
40
50
60
70
Wave length nm.
Visible spectra

Fastness Properties :

Colour fastness of a 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 :

Class :	Grade :
8	outstanding
7	excellent

6	very good
5	good
4	fairly good
3	fair
2	poor
1	very poor

Washing Fastness :

This property is an important consideration for azoic dyes on cotton. The action of boiling caustic soda solution on azoic colour has been extensively studied by Rowe et. al. (71-74). Different workers have tried to generalise the relation between structure of naphthol and washing fastness (75-77).

In the present study the washing fastness for (i) is in the range of 2 to 5, while that for (ii) is in the range of 3 to 5. The acetyl derivatives (iii) and (iv) have less washing fastness than the corresponding hydroxyl derivatives (i) and (ii). The introduction of carboxylic group (compound v) in (i) results in increasing the washing fastness, however, introduction of hydroxyl group (vi) and (vii) results in lowering the fastness. Thus the fastness to washing is varied not only with the groups present in these components, but also with the position occupied by them and the diazo salt used for coupling.

Light Fastness :

Among the properties described in a dye, fastness of light is of impotance. The difficulty in quantitative assessment of fading is that the change involves all the three characteristics of colour, purity (or chroma), brightness (or value in the munsell system) and less frequently, the hue (or dominent wavelength)(78). The light fastness of an azoic dye is dependent on both the components. Light fastness of some of shades of Naphthol ASG are varying from 1 to 2, while for a few shade, they are varying from 7 to 8.

The light fastness properties of compounds 1-hydroxyanthracene, 2-hydroxyanthracene and 1-hydroxyanthracene-2-carboxylic acid are same. They are in the range of 2 to 3. But in case of compounds (iii) and (iv), some increase in light fastness is observed. When p-cl-aniline, 5-cl-o-toluidine, dianisidine are used for developing compounds in (iii), light fastness of very good grade is obtained. Introduction of hydroxyl group in compound (i) at 5 and 8 position (compounds vi and vii respectively), the fastness property increases for some bases, while remains same for other bases. It varies in the range of 2 to 6.

Crocking Fastness :

The nature of the dyeing process indicates that the main problem in azoic 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(79). The rubbing fastness of azoic dyed materials depends upon the substativity of the naphthol towards fibre and the efficiency of the removal of the azoic pigment by the scaping after-treatment.

The rubbing fastness of compounds (i) to (v) are in the range of 2 to 3, and for compounds (vi) and (vii) is 1 to 2. The less rubbing fastness in the last two compounds might be attributed due to more pigment formation on the fibre.

Desai et. al. have studied hydroxy naphthalene derivatives as azoic coupling components(80). Comparision of fastness properties of hydroxynaphthalene and hydroxyanthracene derivatives shows that no appreciable change is taking place as far as washing and rubbing fastness is concerned, but little lowering in light fastness is observed. It is known that fading of dyes by the action of light is usually an oxidation process. Hydroxyanthracene derivatives are [illegible] easily oxidisable than corresponding naphthalene derivatives. So far many dyes having poor fastness to light are giving fluorescence in solution or on the fibre. Azo derivatives of hydroxyanthracene are highly fluorescent in solution. Thus lowering in light fastness can be explained. Fluorescence, fading and dye - sensitized photochemical reactions are process by which observed light energy is dissipated.

REFERENCES

REFERENCES

1. 'Colour Index', 2nd Ed., Society of Dyes and Colourists, Bradford, England and American Association of Textile Chemists and Colourists, Lowell, Mass., (1956).
2. GrE., Brit. Pat. 23732; DR. Pat. 293897.
3. Rowe, F.M. and Levin, E. J. Soc. Dyers Colourists, 42, 207 (1926).
4. Semard, A., Teintex, 4, 76 (1939).
5. Rowe, F.M., J. Soc. Dyers Colourists, 46, 227 (1930).
6. Rowe, F.M. and Levin, E., J. Soc. Dyers Colourists, 40, 218 (1924).
7. GrE., Brit. Pat. 13,237; DR. Pat. 264,527.
8. Ueno, S. and Suzuki, T., J. Soc. Chem. Ind., (Japan), 37, Suppl. binding, 233 (1934),
9. Discrens, The Chemical Technology of Dyeing and Printing, Reinhold, New York, (1948).
10. Fierz, D., Kunstliche Organische Farbstoffe, Erganzungsband, Springer, Berlin, (1935).
11. Diserens, L., Rev. Gen. Mat. Color., 40, 265 (1936).
12. ICI, Brit. Pat. 367, 907; DR.Pat. 549, 983.
13. ICI, Brit. Pat. 343, 164, DR.Pat. 551, 880.
14. ICI, Brit.Pat. 347,113; DR. Pat. 539,116.
15. Rowe, F.M. and Levin, E., J. Soc. Dyers Colourists 41, 355 (1925).

16. Rowe, F.M. and Corbishley, S.G., J. Soc. Dyers [illegible] Colourists, 41, 278 (1925).

17. Rowe, F.M. and Levin, E., J. Soc. Dyers colourists, 42, 82 (1926).

18. Dorman, K.L., Amer Dyestuff, Reptr. 28, 82 (1939).

19. British Intelligence Objectives Sub-Committee Report 1149.

20. British Intelligence Objectives Sub-Committee Report 1363.

21. British Intelligence Objectives Sub-Committee Report 986.

22. Williams, A.F., J. Soc. Dyers Colourists, 50, 204(1934).

23. Blackshaw, H., J. Soc. Dyers Colourists, 51, 399 (1935).

24. Yates, S., The Industrial Chemist, 20, 489, 605, 667 (1944).

25. Adams, D.A.W., J. Soc. Dyers Colourists 67, 223 (1957)

26. Wiasmitinov, A., Textit-Rundschau, 13, 507 (1958).

27. V~~a~~enkataraman, K., "The Chemistry of Synthetic Dyes", Vol.1, Chapter 22, Academic Press Inc. New York, Edition (1965).

28.. Saunders, K.H., "The Aromatic Diazo Compounds and their Technical Applications", Edward Arnold, London (1949).

29. Abrahart, E.N., "Dyes and their Intermediates", Pergamon Press, Oxford, (1958).

30. Trotman, E.R., "Dyeing and Chemical Technology of Textile Fibres", 4th ed., Griffin, London, (1970).
31. Allen, R.L.M., "Colour Chemistry", Nelson, London (1971).
32. Farbwerke, Hoechst A.G., U.K. Pat. 1,062,776.
33. Gross, R., Textil-Praxis, 15, 1046 (1960).
34. Kirst, W., Melliand Textilber, 41, 857 (1960).
35. Staab, W., Melliand Textilber, 44, 978 (1963).
36. Bamberger, R. and Gross, R., Textil-Praxis, 16, 931 (1961).
37. Bamberger, R. and Gross, R., Textil-Praxis, 17, 485 (1962).
38. Farbwerke Hoechst, A.G., U.K.Pat. 951,452.
39. Farbwerke Hoechst, A.G., U.K.Pat. 963,994.
40. I.G.Farbenindustrie A.G., U.K. Pat. 443,222.
41. Farbwerke Hoechst, A.G., U.K.Pat. 1,077,777.
42. France Pat. 1,209,457.
43. Belg. Pat. 5,66,417.
44. Germ. Pat. 1,041,463; 1,067,773; 1,127,322; 1,132,091.
45. Hoechst, A.G., Ger. Offen. 2,552,711; 2,603,445; 2,603,446.
46. Broecker, B., Fiolka, D. and Rath, H., Melliand Textilber, 57, 447 (1970).
47. Shah, N.H. and Upasani, C.B., Colourage, 25(24A), 53 (1978).

48. Shah, N.H. and Upasani, C.B., Colourage, 25(24A), 57 (1978).

49. Iagondinski, K., Ber. dt. Chem. Ges. 39, 1717 (1906).

50. Sircar, A.C., J. Chem. Soc., 757 (1916).

51. Gills, G.H. and Neustadtev, E.L., J. Chem. Soc., 918 (1952).

52. Jadav, N.D. and Shah, N.H., Indian J. Appl. Chem., 35, (4-6), 111 (1972).

53. Ciba, Brit. Pat., 515, 381.

54. Banso, V., Saito, I. and Miyamate, T., Kogyo Kagaka Zasshi 67(i), 177 (1964).

55. AbdEl-Gawad, I.I., Khalil, A.M., Tawfik, N.I., About-Fetouh, M.S. and Al Rifaie, H.O., The Indian Textile J. 88(7), 137 (1978).

56. About-Fetouh, M.S., Tawfix, N.I., Khalil, A.M., AbdEl-Gawad, I.I. and El-Rifaie, E.A., The Indian Textile J. 88(8), 73 (1978).

57. Schmidt, R.E., Ber. dt. Chem. Ges., 37, 66 (1904).

58. Dienel, H., Ber. dt. Chem. Ges., 38, 2862 (1905).

59. Perkin, A.G. and Whattam, T.W., J. Chem. Soc., 122, 289 (1922).

60. Perkin, A.G. and Hall, J., J. Chem. Soc., 123, 2031 (1923).

61. Lele, S.S., Shah, N.H. and Sethna, S., J. Org. Chem., 21, 1293 (1956).

62. Liebermann, C.T. and Hoermann, O., Ber. Dt. Chem. Ges., 12, 589 (1909).

63. Shah, N.H. and Sethna, S., J. Org. Chem., 24, 1783 (1959).

64. Laska, L. and Haller, O., Ger. Pat. 559,333, Chem. Abstr., 27, 735 (1933) .

65. Lampe, Br., Ber. dt. Chem. Ges., 42, 1413 (1909).

66. Technical Manual of The American Association of Textile Chemists and Colourist, 46, 150 (1970).

67. Technical Manual of the American Association of Textile Chemist and Colourist, 46, 126 (1970).

68. Technical Manual of The American Association of Textile Chemist and Colourist, 44, 116 (1970).

69. Morgenstern, J. and Duclos, J., J. Prakt. Chem., 315(6), 1099 (1973).

70. Venkataraman, K.,"The Chemistry of Synthetic Dyes," Academic Press, Inc. N.Y., Vol. 1, p.415 (1962).

71. Rowe, F.M., J. Soc., Dyers Colourist, 47, 29 (1931).

72. Rowe, F.M. and Ueno, S., J. Soc., Dyers Colourists, 47, 35 (1931).

73. Rowe, F.M. and Peters, A.T., J. Soc., Dyers Colourists, 47, 163 (1931).

74. Rowe, F.M. and Giles, C.H., J. Soc. Dyers Coloursits, 51, 278 (1935).

75. Blackshave, H., J. Soc. Dyers Colourists, 52, 9 (1936).

76. Rath, J., J. Soc. Dyers Colourists, 44, 10 (1928).

77. Forster, R.B., Mehta, P.R. and Venkatraman, K., J. Soc. Dyers Colourists, 54, 210 (1938).

78. Seiber, J., Amer. Dyestuff Reporter, 34, 272 (1945).

79. Forster, R.B., Ramachandran, S.R. and Venkataraman, K., J. Soc. Dyers Colourists, 54, 216 (1938).

80. Desai, R.D., Desai, B.M. and Desai, R.M., J. Sci.Ind Res., 14B, 498 (1955).