SYNTHESIS AND APPLICATION OF DISAZO ACID DYES

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AHMADU BELLO UNIVERSITY, ZARIA

DECEMBER, 1999

DECLARATION

I declare that this thesis entitled "**SYNTHESIS AND APPLICATION OF DISAZO ACID DYES**" is my own work and has not been submitted in any form for another degree or diploma at any other university or institution. The information derived from the published work of others have been duly acknowledged in the text by means of references.

M. B. Musa

22/07/00
Date

CERTIFICATION

This is to certify that this thesis work has been prepared in accordance with the regulations governing the preparation and presentation of thesis in the post-graduate School, Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to *Aishatu (Uwa) Musa, Ruqayyat Yakubu* and *Farida Mustapha*, who were victims of unfortunate circumstances.

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ABSTRACT

Disazo dyes of the type $A^1 \longrightarrow Z \longleftarrow A^2$ were prepared by diazotization and coupling. The characterization and spectrophotometric analysis of the derived dyes were carried out. The synthesized dyes were applied to wool, polyamide and cotton fabrics, and the dyeing properties investigated.

It was shown that the disazo dyes exhibit bathochromic shifts within the visible absorption band, as compared to the monoazo dyes derived from similar primaries, due to increase in conjugation and molecular size.

Most of the dyes exhibited bathochromic shifts as the solvent polarity was increased. Similarly, most of the dyes showed positive halochromism.

The dyes were found to be substantive to wool and polyamide with good fastness properties.

CHAPTER ONE

1.0 REVIEW OF LITERATURE

Dyes are coloured substances which when applied to a substrate impart colour to this substrate by a process which at least temporarily destroys any crystal structure of the coloured substances. The dyes are retained in the substrate by adsorption, solution and mechanical retention or by ionic or covalent chemical bonds.

Dyes and pigments owe their colour to the presence of substances that absorb light of wavelength ranges within the visible region of the electromagnetic spectum (400 - 700nm). This is as a result of the electronic transmissions between various molecular orbitals of the molecule. The energy differences between the orbitals determine whether the "colour" falls in the visible range of the electromagnetic spectrum and, if it does the precise shade or hue.

Every dye or pigment therefore exhibits a characteristic colour arising from its chemical structure. However, the colour seen for a given coloured substance is the reflected (complementary) colour(s), the substance having absorbed particularly wavelengths within the visible spectrum.

Table 1.1 shows the pairs of complementary colours and wavelengths absorbed([1])

TABLE 1.1.: PAIRS OF COMPLEMENTARY COLOURS

COLOUR ABSORBED	WAVELENGTH ABSORBED(nm)	COLOUR SEEN	WAVELENGTH ABSORBED (nm)
VIOLENT	400-435	Yellow-green	560-580
BLUE	435-480	Yellow	580-595
GREENISH-BLUE	480-490	Orange	595-605
BLUISH-GREEN	490-500	Red	605-750
GREEN	500-560	Purple	400-435
YELLOW-GREEN	560-580	Violet	435-440
YELLOW	580-595	Blue	435-480
ORANGE	595-605	Green-blue	480-490
RED	605-750	Blue-green	490-500
PURPLE (Red+Violet)	400-435	Green	500-560

The absorption spectrum of a dye may be complex, and the purity of the colour observed depends on the shape of the absorption spectrum curve of the dye. Bright colours are the result of narrow absorption bands with sharp peaks. Non-spectral colours such as brown are associated with absorption spread fairly evenly over a wide wavelength range, and black is the result of absorption throughout the visible spectrum.

It is worthy of note that, many substances absorb radiation of wavelength above and below the visible range, and the fact that such absorption does not give rise to a coloured appearance is due to the limited sensitivity of the eye rather than to any difference in principle.

In order to explain the above observation, Young-Helmohozt theory[10] assumes that the human eyes possesses three types of receptors. These receptor cells respond to red, green and blue or violet colours. The conversion of light energy into electrical energy takes place in the retina of the eye where sensitive tissues, of the rods and cones are embedded. The inability of these tissues to respond to electromagnetic waves of wavelength is responsible for the colourless appearance.

1.2 BRIEF HISTORY OF DYES

In the early days natural dyes and mineral pigments were used to colour various materials, such as furs, textiles and other objects. These colouring matters are mainly obtained from vegetables and also may be obtained from animals. The use of indigo and woad (C.I. Natural Blue 1) has the oldest record of use. Sanskrit[1] writing show that over four thousand years ago, the cloth wrapping of Egyptian mummies were dyed with indigo.

Ancient Egyptian hieroglyphics contain a thorough description of the extraction of natural dyes and their application in dyeing.[32] The extraction procedure for the natural dyes is somehow cumbesome and expensive for large scale production. The natural dyes have no affinity for textile fibre and always require a mordant for their fixation to the fabric, which gives colour depending on the particular metal from which

the salt is made. Therefore, at the later part of the 19th century, the natural dyes industry was gradually suspended by the new synthetic dyes.[6]

The discovery in 1856 by W.H. Perkin of the dye mauve, or mauveine virtually marked the beginning of the synthetic dye industry. It was an accident discovery (a serendipity) which occured when Perkin was trying to synthesize quinine through the oxidation of mixture of aniline bases. In the course of the oxidation reaction a black precipitate was obtained which after extraction with alcohol resulted into a purple dye instead of the expected quinine. The brilliant violent hue of mauve on silk immediately stimulated the attention of many chemist and in 1859, E. Vergum in Lyon discovered Fuschine[2]. During the decade following the discovery of mauveine the dyes magenta, rosanilline blue, methyl violet, Hofmann violet, Aniline black and Aldehyde green were discovered.[7]

Prior to the discovery of the mauveine, other synthesized dyes were actually in record though without any industrialized processes. Picric acid, which was obtained by Woulfe in 1771[2] by treating indigo with nitric acid, was used for dyeing silk yellow, but did not attain any significance. For this reason, probably, W.H. Perkin, not Woulfe, was given credit for having produced the first synthetic organic dye.

The decisive work by August Von Kekule on the quadrivalence of carbon (1858) and on the constitution of benzene (1865),[2]. Opened the way for the planned preparation of

purely synthetic dyes, as well as for the artificial production of natural dyes. With this discovery the research into the development of the synthetic dyes became more directional and gave rise to the elucidation of already proven dyes as well as the development of analogues of some natural dye-stuffs.

The synthesis of alizarin was achieved in (1868) by Graebe and Liebermann[12]. BY 1868, Perkin in collaboration with Caro, Graebe and Liebermann[3] improved and patented alizarin having developed improved methods of synthesis. They were also able to produce one tonne of the dye at the time. Perkin was able to reach an annual production capacity of four hundred and thirty tonnes by 1873.[3] The discovery by P. Griess, in 1858 and 1864 of the diazotization reaction of aromatic amines and the coupling reaction of diazonium compounds in addition to the elucidation by Kekule in 1865 of the structure of benzene ring laid the basis for the next important phase in the development of the dye industries.

The period from 1870 to 1910 marked the classical period of dye chemistry due to the amazing discoveries of dyes as listed in the Colour Index. By 1910 most of the main classes of dyes had been established, and the subsequent advances were developments.

The major discoveries since the early 1900s have been disperse dyes, which were initially used for cellulose acetate but are now also used widely for other synthetic fibres, phthalocyanine dyes and finally fibre-reactive dyes[2] than followed Clavel and Dreffuss[17] solved the problem of lyeing hydrophobic fibres by means of disperse dyes. The post-war era is characterised by the development of pigments which achieved importance for colouring plastics, example of which include quinacridone[5], chromophthalic pigments[3]

In 1951-52 reactive dyes for wool were developed[10] Typical examples include Remalan and Cibalan produced by Ciba and Procion dyes produced by ICI. These give very brilliant shades on the substrate and the fastness characteristics are very excellent

1.3 THE BASIS OF COLOUR IN ORGANIC COMPOUNDS

Dyes are characterised in accordance with their capacity to absorb the energy of that part of electromagnetic radiation to which the human eye is sensitive. Absorption of the relatively low-energy microwave and infrared radiation is associated with changes in the rotational and vibrational energy of molecules and atomic groups. However, the higher energy of visible and ultraviolet light raises the electrons into excited state. There is therefore no fundamental difference between visible and ultraviolet spectra.[1]

Several chemical theories discussing the relationships between chemical constitution and colour of organic compounds

were postulated. Graebe and Liebermann,[13] (1868) observed that all organic dyes were decolorised on reduction, indicating that the colouring matter had to be unsaturated to be able to emit colour, O. N. Witt in 1876 extended this view by pointing out that the colour of organic dyes is associated with the presence of chromophores[14], and that the compounds behave as dyes only when they contain auxochrome.[19] However, in order to dye efficiently and intensify colour, Nietzki's rule[21] (1897) proposed that the introduction of substituent weighing groups e.g. methyl, phenyl, ethoxy, bromo, nitro etc. deepened the colour of a given dye as its molecular weight is increased; however, there are many exceptions. Hewitt and Mitchell[22] state the rule correctly in terms of the dependence of colour on the conjugation length in a molecule. Schutze[23], in 1892, examined Nietzkis rule in depth pointing out many exceptions and in so doing coined the terms bathochrome and hypsochrome. These are now used to describe red (bathochromic) and blue (hypsochomic) shifts in absorption spectroscopy.

The next major development was the quinonoid theory advanced by Armstrong[24], who pointed out that most dyes can be represented in a quinonoid form since quinones were known to be components of several colours. Armstrong[24] did not explain the reason why they gave rise to colour. Bayer[25] in 1907 put further the view that colour might be due to "rhythmic" vibration caused as a result of oscillation of the quinonoid condition between two benzene rings. Burry[26] in 1935

attributed the colour observed to the movement of electrons which give rise to two distinct but identical structures. He described dyes as resonance hybrids of classical structures of similar stability but different charge distribution.

With theory, scientists began to consider colour and constitution from the stand point of the resonance theory.

RESONANCE THEORY IN RELATION TO COLOUR

Burry (1935)[26] pointed out that the majority of dyes existed in resonance hybrids i.e. a compound having two extreme structures, but in between the extreme structures are some intermediate energy. The closer the two forms are in energy, the smaller will be the gap between the ground and first excited states i.e. the more bathochromic will be the light absorption band, e.g.

$R_2N-(CH=CH)_nCH=N^+R_2$ <-------> $R_2N^+=CH-(CH=CH)_n-NR_2$

(a) (b)

Fig. 1.2

The two structures (a) and (b), are equal in energy and thus resonance theory suggests that these should absorb at longer wavelength.

However, the main weaknesses of the resonance theory lies in the assumption that only a few, low energy canonical forms contribute to the hybrid molecular structure. It has been found out that various high energy forms may make an important contribution to the excited state of a molecule; neglect of this can lead to the prediction of high energy absorption band where in fact low energy transitions exist.

Example here is shown in c, d, and e. A and D are acceptor and donor groups respectively. It is observed that the relative order of Amax values for these systems will be e>d>c. The reverse order is predicted by the resonance theory.

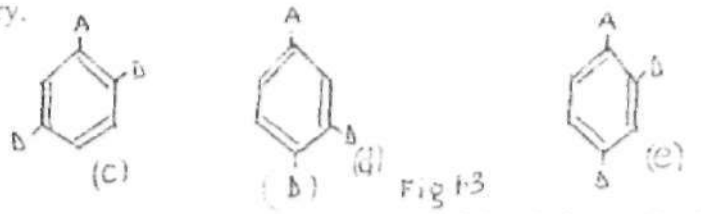


Fig 1-3

The resonance theory is very useful only in qualitative prediction of colour-structure relationship. However, the quantitative treatment has been approached with greater success by the molecular orbital methods.

MOLECULAR ORBITAL METHOD IN RELATION TO COLOUR

The molecular orbital method assumes that a molecular orbital is formed by the overlapping of outer single occupied orbitals of two or more atoms, resulting to several types of molecular orbitals. This is called the linear combination of atomic orbitals (LCAO) method[27]. Each molecular orbital has a characteristic shape, size and energy and are denoted by symbols such as σ, σ^*, π, π^* bonding and antibonding orbitals.

Atomic orbital that are incapable of combination such those containing inner shell or lone pair electrons are described as non-bonding n-orbitals. In the ground electronic state of most organic molecules all the bonding and non-bonding orbitals are fully occupied while the antibonding orbitals are empty. 28 Absorption of a quantum of energy of a wavelength within the visible region a σ,π bonding electron associated with a covalent bond or a non-bonding (n)

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electron to be promoted to an empty antibonding level, thus bringing about the excited state.

In simple molecules, the electronic energy - level are in the order $\sigma < \pi < n < \pi' < \sigma^*$ (Fig. 1.4). Transition of the type *n ---->π' normally give rise to spectral bonds at longer* wavelengths than those due to transition π--->π' or σ--->'σ (in the uv region). In the dye molecules the π-->π' is more probable since there are as many π levels as there are conjugated atoms. The energy gain ΔE is in the first approximation equal to the energy difference between the two molecular orbitals concerned in the transition and is related to the wavelength (λ) of the light absorbed by the equation;

$$\Delta E = Ew_A - Ew_D = \frac{hc}{\lambda} \quad ----(1)$$

where,

w_A & w_D = acceptor and donor orbitals wavefunciton respectively.

h = Planck's constant.

c = Velocity of light.

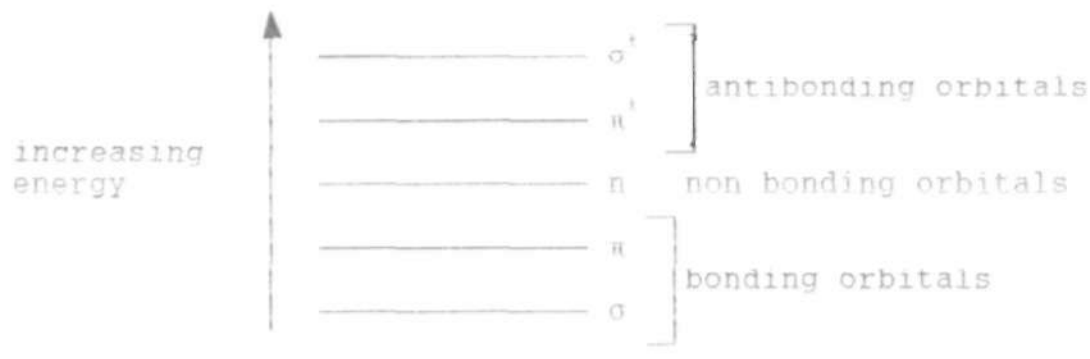


Fig. 1.4 Energy levels in dye molecule.

1.4 CLASSIFICATION OF DYES

Dyes and pigments may be classified according to various systems; however, two most important and common systems are the classification according to (A) constitution of chemical structure and (B) methods of applications.

A.] CLASSIFICATION OF DYES ACCORDING TO CONSTITUTION

i.) ANTHRAQUINONE DYES:

The characteristic chromophoric group present in authraquine series consist of one or more carbonyl groups in association with conjugated systems, one of which is an aromatic nucleus or condensed ring of it.

e.g.

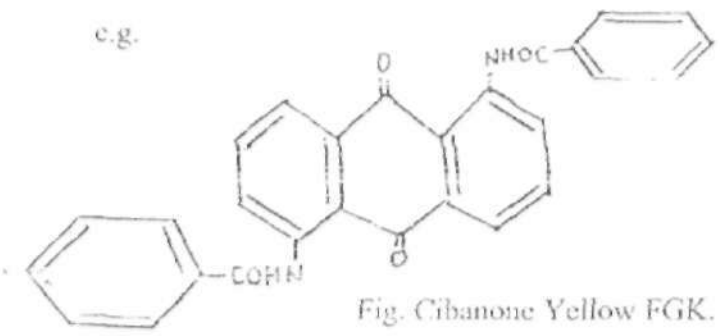


Fig. Cibanone Yellow FGK.

Anthraquinone is a faintly coloured compound and does not posses dyeing properties until it is being introduced with electron donors such as -OH, NH_2, NR_2, NHAr etc (Fig. 1.5). These electro donors also provide the compound with the ability to absorb in any desired region of the visible spectrum, thus it is possible to have yellow, red, blue, and green anthraquinone dyes. They are often synthesized by cyclisations and reduction reactions between components containing several reactive positions. Consequently, some of the commercial products of anthraquinone dye are *mixtures* [29]

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i) NITRO DYES:- These are phenols or amines containing the nitro (NO_2) group in the ortho or para positions in conjunction with aromatic residue. The water soluble members of the series are acid colours while insoluble members are pigments. The nitro chromophoric group is often found in dyes having different chromophoric groups. In a few dyes however, the nitro group is the only chromophore and OH or NH_2 is present as auxochrome and resonance between one of two tautomeric forms gives rise to colours e.g. picric acid gives greenish yellow on silk.[5]

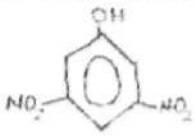


Fig. 1.6 PICRIC ACID

iii) NITROSO DYES: The characteristic feature of the nitroso dyes is the presence of nitroso (NO) chromophoric group in conjunction with aromatic group.



They are prepared by the nitrosation of aromatic compound. e.g.

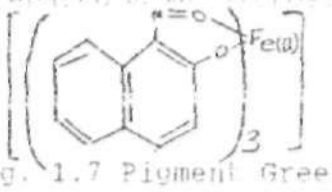


Fig. 1.7 Pigment Green B

iv) TRIARYL METHANE DYES:- These dyes are characterised by their chromophoric system consisting of central carbon atom linked to three aromatic groups usually containing two to three substituted amino groups e.g.

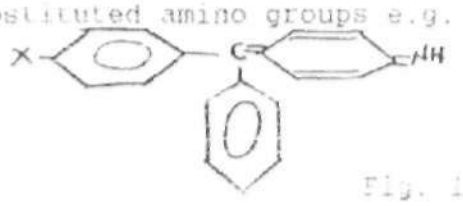


Fig. 1.8

The hue and the dyeing properties depends on the nature and number of auxochromic groups such as OH, NR_2, NHR, NH_2, or combination of these in the three-para positions. All the dyes in this group are derived from the triphenylmethane; they can also be synthesized by condensation of benzene with carbontetrachloride to form the aluminium complex of triphenylmethane chloride which is then reduced to hydrocarbon by heating.

v) METHINE, POLYMETHINE AND CYANINE DYES:- These are characterised as a group due to their chromophoric system of an acrylic link of methine group (-CH-) They are mainly employed as photographic sensitizers in colour photography. They have only limited use on textiles. E.g. Bixin serves as food and drug colorant.

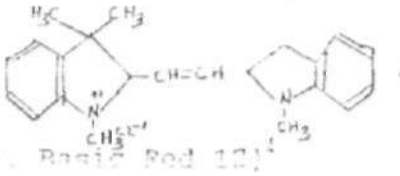


Fig. 1.9 (C.I. Basic Red 12)

vi) SULPHUR DYES:- These are obtained by heating certain organic compounds with sulphur linkage serving as the chromophore within the dye molecule. The resultant compounds have high molecular mass but with undefined structure. e.g. vidal black.

vii) INDAMINE AND INDOPHENOL DYES:- Consist of derivatives of benzoquinone mono or diamine or corresponding naphthalene compounds. Dyes of this class are mainly used for colour photography and also as intermediates for sulphur dyes e.g.

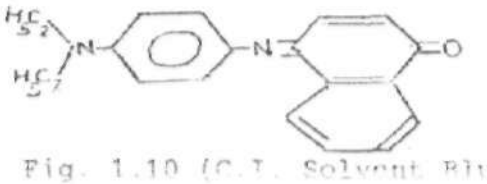


Fig. 1.10 (C.I. Solvent Blue 22)

viii. **STILBENE DYES:**

Characterised by the presence in their structure of the stilbene residue.

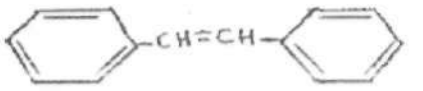


Fig. 1.11

The first stilbene dye was discovered by Walter[30] (1963) and is still manufactured by many firms under different names. It gives yellow shade of low fastness to light, and is used for dyeing and printing of papers. It is also used in fluorescence brightining.

ix. **AZO DYES:**

Account for over 60% of available dyes known to be manufactured. They are characterised by the presence of one or more Azo chromophoric groups in the dye molecules which forms bridges between organic molecules one of which is usually an aromatic nucleus.

They are usually synthesized by diazotization of aromatic primary amines which is subsequently coupled with a suitable coupling component, which may be a phenol, napthol or aromatic amine having a free ortho and/or para positions or certain other compounds having reaction groups. e.g.

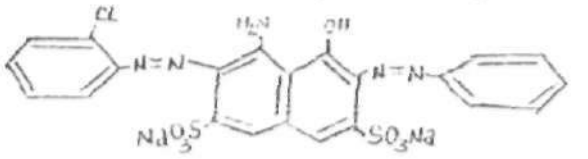


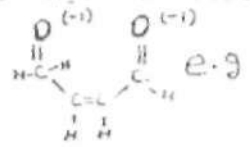
Fig. 1.12 A Typical Azo Dye.

Other less important classes of dyes includes:-

x. **PHTHALOCYANINES:**

Comprises of ring system of indole units and nitrogen atoms. It combines with various metals to form coloured compounds. They have brilliant colours and excellent heat fastness.

xi) INDIGOID AND THIOINDIGOID DYES:- Two units of indole or thionaphthene are linked to form a dye molecule. The chromophoric group is represented by



e.g

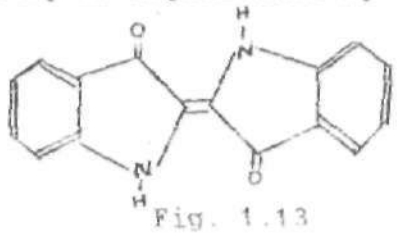


Fig. 1.13

xii) THIAZINES:- Contain phenoxazine derivatives e.g.

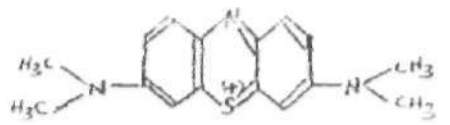


Fig. 1.14 Methylene Blue.

xiii) OXAZINES:- Contain phenoxazine derivatives e.g.

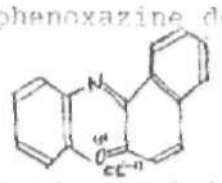


Fig. 1.15 Meldola's Blue.

xiv) ACRIDINES:- Salts of 9-hydroxy-9,10-dehydroacridine with amino groups in 3,6 positions.

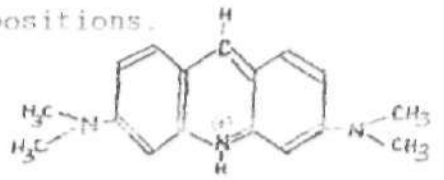


Fig. 1.16 Acridine Orange NO

xv) THIAZOLES:- Aminothiazole or azothiazole sulphonic acid, or thiazolinium salt. e.g.

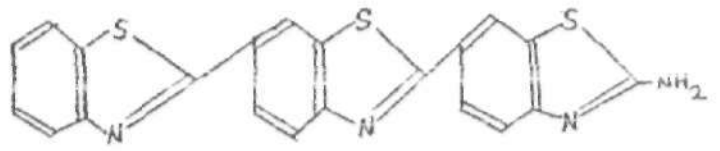


Fig. 1.17

B. CLASSIFICATION OF DYES ACCORDING TO APPLICATION

The practical dyer is interested in classification according to application i.e. according to the ability of the dyes to dye various fibres. There are two important groups.

I. Classes of dyes that are absorbed from aqueous solution. The process is reversible i.e. desorption of the dye can occur, although the ease varies greatly.

They include the following classes of dyes.

i) DIRECT DYES:- They are directly substantive to cellulosic fibres, and are usually applied to cotton fibres from aqueous solution containing electrolyte. They are high molecular weight compounds. However, they have low wet fastness properties; therefore, after treatment is applied to improve fastness properties.

Planarity in a molecule and linearity are important requirement for substantivity to cellulosic fibres. The presence of too many ionized groups in the direct dye molecule lower its substantivity and hence its wet fastness properties; the number of solubilized groups should be the minimum required for water solubility. The aromatic rings in the dye molecule should be co-planar. e.g.

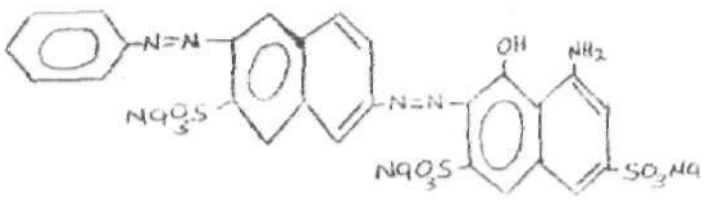


Fig. 1.18 a Typical Direct Dye.

Direct dyes are further subdivided into three classes.

Class A:-Have good migration properties, high leveling power. They may be uneven initially but further boiling brings about even distribution.

Class B:-(Salt Controllable) have poor levelling power, Exhaustion is brought about by controlled addition of salt. If not level at initial stage, it is difficult to control levelness.

Class C:-Are not self levelling. They are very sensitive to salt, and they require addition of salt and control of temperature to control exhaustion.

After-treatment is carried out to improve wet (and/or light) fastness properties and this is achieved by increasing the size of the dye molecule inside the fibre.

ii. **ACID DYES:-**

They are largely sodium salts of sulphuric acids with usually two to three sulphonic acid groups in the dye molecule. But there are a few containing carboxylic groups. They are applied to nitrogenuous fibres such as wool, silk, and nylon, all of which contain basic groups. Acid dyes are usually applied from acid dyebath, or sometimes from neutral dye bath.

Acid dyes for wool are classified into three groups according to their dyeing and wet fastness properties.

GROUP A:-LEVELLING ACID DYES; (Sometimes called equalizing dyes) have fairly simple chemical structure, migrate readily on wool, and are easily applied from strong acid bath. They have low wet fastness properties due to their relative low molecular weight.

GROUP B:- MILLING ACID DYES; are structurally more complex, have high affinity and are applied from weakly acid baths for control of the rate of dyeing but they show high fastness to milling and other wet treatments.

GROUP C:- They are characterised by high anion affinity and therefore have poor levelling or migration properties. They are referred to as neutral dyeing acid dyes or super milling dyes on account of the high fastness to milling. Adequate control of pH is very important in their application. The low acidity required is attained using an acid liberating salt such as ammonium acetate or ammonium sulphate. The dyeing produced with dyes in this group has good wet and light fastness.

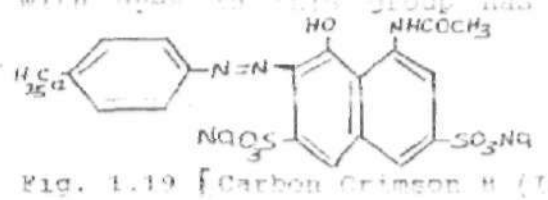


Fig. 1.19 [Carbon Crimson H (ICI)][15]

iii) BASIC DYES:- They are coloured cations in aqueous solution, therefore referred to as cationic dyes. They have affinity for protein fibres and cellulosic fibres mordanted with tannic acid. They are characterised by the presence of a basic ammonium group.[1] It may also be present as a part of a heterocyclic ring as a tetracovalent atom, hence triphenyl methane dyes, xanthenes, acridenes, oxazines and thiazines are considered or are used as basic dyes.

iv) DISPERSE DYES:- Are only sparingly soluble in water and are applied from finely dispersed particles in aqueous solution. They are used for the colouration of cellulose acetate and

polyesters. They are monionic, crystalline when pure and have low molecular weight. When heated above melting point they sublime without decomposing. Chemical grouping in the dyes responsible for solubility are normally those which can form hydrogen bonds with water, notably - N=N, OH, $-NH_2$, -O-, Alkyl, -NH-

Example of a disperse dyes is shown below:-

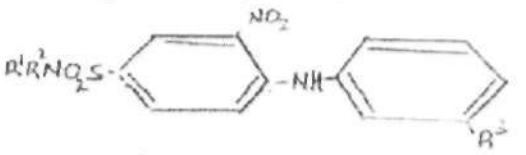


Fig. 1.20 A Typical Disperse Dye.

II.] Classes of dyes, the characteristic features of which is that the state of the dyes in the finished material is such that desorption is only under conditions which is rarely encountered during subsequent processes or use. They exhibit high fastness properties.

These groups of dye are further divided into three classes.

A.] All classes of dyes in the final state of which, the colourant is present inside the fibre in the form of large particles insoluble in water and most of the liquid with which the material is likely to come into contact with during processing or muse. It gives dyeing and prints of a very high wet fastness.

I. **SULPHUR DYES:-**

Used mainly for dyeing cellulosic fibres. They are insoluble in water and therefore solubilized by alkaline reduction before dyeing. They include conventional sulphure dyes, leuco-

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sulphure dyes, solubiized sulphur dyes and condensed sulphure dyes. After application they are usually oxidized into an insoluble colourant inside the fibre.

II. **VAT DYES:-**

The dyes are insoluble in water and therefore converted to solubilized leuco form by treatment with sodium dithionite. After application, the dye is reoxidised to insoluble pigment inside the fibre, by exposure to air. An example of Vat dye is shown in fig. 1.21.

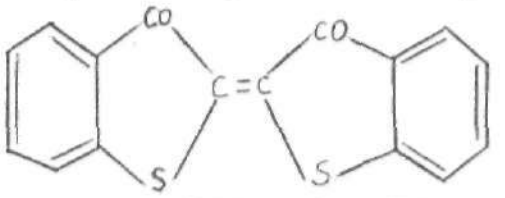


Fig. 1.21. THIOINDIDO VAT DYE

III. **AZODIC DYES:-**

Applied to cellulosic fibres by first impregnation with a solution of sodium salt of the coupling component and then subsequently passed through a solution of diazotised amine, so that the highly coloured insoluble Azo compound is formed inside the fibre.

IV. **MORDANT DYES:-**

These are acid dyes which contain in their molecules suitably orinted chemical groups which can form complexes with metals particularly chromium, hence also referred to as chrome dyes.

B. **REACTIVE DYES:-**

These form chemical covalent bonding with the fibre. The functional groups of fibre, that react with reactive dyes to form the covalent bonds are the hydroxyl groups of the cellulose and the amino, carboxyl, hydroxyl and thiol groups of wool, and nylon. All these residues have a nucleophilic character

and therefore add to the electrophilic centre of the reactive group.

Other forms of reaction of fibre with reactive dyes under alkaline condition is nucleophilic substitution.

Other reactive dyes react under acid conditions.

Example of reactive dye.

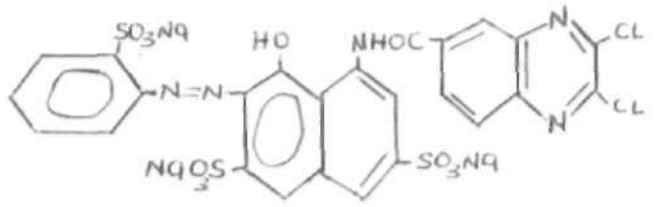


Fig. 1.22 Levafix E dye.

C) PIGMENT:- These are insoluble in water and most organic solvents from which medium they may be applied. They can be introduced into the textile fibre during fibre manufacture by mixing them with the fibre forming material prior to extrusion to form the filament. For some fabric they are applied using resin-pigment method.

1.5 RAW MATERIALS FOR DYE SYNTHESIS

Pure chemical substances used as raw materials for the manufacture of dyes are referred to as primaries. The most important of them are benzene, toluene, the xylenes, phenol, the cresols, naphthalene, anthracene and carbazole. Although aromatic compounds are present in petroleum the content is usually so low that they cannot be isolated economically. Borneo petroleum is exceptional in containing as much as 40% of aromatic hydrocarbons. The petroleum industry has developed several processes whereby aromatic compounds are obtained from

non-aromatic fractions. The first of these were cracking processes, which were designed to bring about the cleavage of high-boiling components into more volatile fractions but which with the aid of suitable catalysts also enable naphthenes to be dehydrogenated with formation of aromatic products. The application of these processes was limited by the content of suitable precursors in the natural oil, and they were chiefly of value for the production of fuel of increased octane rating. Later various reforming processes were developed, making use of a wider range of aliphatic compounds and yielding lower - boiling aromatic products. Thus benzene is obtained by dehydrogenation of cyclo paraffins (with removal of side chains where necessary), by dehydrogenation with molecular rearrangement of methylcyclopentane or by dehydrogenation with cyclisation of n-hexane. Toluene is produced by several analogous processes, for example by dehydrogenation of methylcyclohexane[21] in the presence of catalyst (molybdena-alumina platinum, cobalt, molybdate or chrome-alumina).

The catarole process developed by petrochemical limited converts paraffinic hydrocarbons at 630-680c by means of copper or copper-iron catalyst into a liquid product (36-54% feedstock) which is almost entirely aromatic and a gas consisting mainly of ethylene and propylene. The aromatic products are essentially the same as those obtained from coal tar and compounds of lower molecular weight predominate.[24,25]

The proportions of benzene, toluene and the xylenes in the total production from petroleum are about 1:1:1, but the commercial demand is for a much higher amount of benzene. Several processes have been devised for demethylating toluene and xylene, either of which can be converted into benzene and methane by reaction with hydrogen in the presence of a catalyst, such as chromium trioxide on alumina or platinum on alumina. The thermal hydro dealkylation process (Gulf Research and Development Co.) is stated to convert toluene into benzene with atleast 95% efficiency without a catalyst.[16]

By means of reactions such as nitration, reduction, halogenation, sulphonation, oxidation, carboxylation, amidation, hydrolysis, caustic fusion, or friedel-craft reaction, the primaries are converted to intermediates which by further reactions yield dyes. The intermediates are usually colourless substances. However, it is not unusual for a dye (especially azo dye) to be converted by one or more further reactions into a more complex dye.

1.6 SYNTHESIS OF AZO DYES

The importance of azo dyes is shown by the fact that they represent the largest group of industrial dyes. They account for over 60% of the total dye structures known to be ~~the~~ manufactured, and many classes of dyes are represented. They cover the whole visible region of the spectrum, thus yellow, red, blue, green, black etc are obtained.

Azo dyes are compounds containing one or more azo groups (-N=N-) in their molecules, which form bridges between organic residues, of which atleast one is an aromatic nucleus. There are monoazo, disazo, trisazo, tetrakisazo and polyazo dyes according to whether there are one, two, three, four, or more azo groups present in the dye molecule.

The advantage of using azo (-N=N-) links is to connect groups which are themselves not coloured e.g. benzene, naphthalene rings etc to produce a coloured molecule or dye.

By extending the conjugation (alternate double and single bonds), the azo links build up the wavelength of absorption throughout the visible region, thus generating colour.

1.6.1 PRINCIPLES UNDERLYING THE PREPARATION OF AZO DYES

Among the methods for producing aromatic azo compounds, azo coupling, i.e. the reaction of an aromatic diazo compound with a coupling component, is of outstanding significance.

The diazo or diazonium salt is obtained by "diazotisation" of a primary aromatic amine. The diazo compound is then coupled with a second substance, usually a phenol, a naphthol, an enolizable ketone or an aromatic amine, an azo compound being formed. The participating molecules are known as diazo component and coupling component respectively.

1.6.2 DIAZOTIZATION

The diazotization of aromatic primary amines is the first of two reaction steps by which practically all azo dyes are produced. An aqueous solution of the amine is converted into

the diazonium ion at a temperature of about 0^0c by the action of a mineral acid.

$$Ar - NH_2 + 2HX + NaNo_2 \longrightarrow Ar - N_2^+x^- + Nax + 2H_2O$$

where X = Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^- etc

The use of at least two (usually 2.5) equivalents of the mineral acid (Hx) in accordance with the above equation is essential for smooth reaction, this is a consequence of the equilibria that exist.

A diazonium salt is formed when a primary aromatic amine is acted upon in aqueous acid medium by nitrous acid, and the amine is said to have been diazotised, a second nitrogen atom having been introduced into the molecule. The reaction may be envisaged as taking place thus;

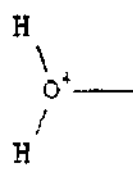
$$Ar.NH_2 + HNO_2 \xrightarrow{(a)} Ar.^+NHNO \longrightarrow Ar.NH.NO \longrightarrow$$

$$\longrightarrow Ar.N{=}N.OH \longrightarrow Ar.N^+ \equiv N \longleftrightarrow Ar\ N{\equiv}N^+$$

where Ar represents an aromatic hydrocarbon radical. Reaction (a) is the rate determining step and is in effect a nitrosation of the amine.

The mineral acid commonly used in diazotisation in most cases is HCl.

The actual nitrosating species varies according to conditions and may be:

N^+O, NOCL,  or N_2O_3

At low acidities, it is probable that N_2O_3 is the effective agent.

The replacement of hydrogen and primary aromatic groups by the nitroso group (diazotization) is of special importance in the dyestuff chemistry. The diazonium ion thus arising acts as electrophilic component in azo coupling. This is the most important reaction in the production of azo dyes.

1.6.3 EFFECTS OF SUBSTITUENTS IN DIAZOTIZATION

The nature and position of substituents in the nucleus as affecting the basicity of the amine determine the readiness with which an aromatic amine may be diazotised. Thus, p-nitroaniline and 2,4-dinitroaniline are much less basic relative to aniline because of the electron-withdrawing NO_2 group(s) and infact, require special methods for their diazotisation. Diazotisation of weakly basic amines like 2,4-dinitroaniline and 1-aminoanthraquinones is carried out by adding the solid amine to nitrosylsuphuric acid.

Diazotisation becomes difficult through low solubility of the aromatic amine in aqueous acid, the presence of easily replaceable groups such as - SO_3H, -NO or the presence of easily oxidizable groups such as -OH -CHO. Accordingly a number of methods have been devised to overcome these difficulties.

1.6.4 PRACTICAL METHODS OF DIAZOTIZATION

i) DIRECT METHOD:- Amines which are readily soluble in dilute acids e.g. aniline and certain derivatives of aniline are diazotised using this method.

The amine is dissolved in $2\frac{1}{2}$ - 3 equivalents of acid, then cooled to 0 - 5^0c using ice and the theoretical quantity of sodium nitrite is now added as an aqueous solution over 30 minutes.

Direct diazotisation is accomplished in some cases with a suspension of amine hydrochloride, provided it is in a sufficiently fine form.

A considerable excess of acid (6-7 equivalents) is required for the diazotization of amines like p-nitroaniline. Concentrated sulphuric acid can also be used as reaction medium instead of HCl (concentrated), the nitrosating agent being nitrosylsulphuric acid. Also diazotization can be carried out with glacial acetic acid using amyl nitrite.

2) <u>SUSPENSION METHOD</u>:- This method is used when the amine salt is sparingly soluble in dilute acids, but very soluble in hot concentrated acids. E.g. p-nitroaniline & p-nitro, o-chloroaniline.

The amine is dissolved in hot concentrated HCl and cooled rapidly by the addition of ice to obtain a fine suspension of the amine hydrochloride, then 1-equivalent of sodium nitrite is rapidly added to this suspension at 0-5^0c, when rapid diazotization occurs.

3) <u>INVERSE (INDIRECT) METHOD</u>:- The inverse method of diazotization is employed when the amine salts are insoluble in acids but soluble in alkali. E.g. amine sulphuric acids such as sulphanilic acid and naphthionic acid.

The amine is dissolved in alkali such as dilute NaOH or Na_2CO_3. Sodium nitrite is then added to the aqueous solution of sodium arylamine-sulphonate and the mixture run into a well stirred mixture of ice and dilute acid at (0-5°c). Nitrous acid is generated and the amine is slowly precipited and diazotised.

In the case of naphthionic acid a "zwitterion" or internal salt is formed.

4) DIAZOTIZATION OF VERY WEAKLY BASIC AMINES:- Amines like 2,4-dinitroaniline are made very weakly basic by the effect of electron withdrawing groups present. Such amines are insoluble even in hot HCl, the acid used for these amines is nitrosyl sulphuric acide ($NO^+HSO_4^-$) obtained by dissolving $NaNO_2$ in cold concentrated sulphuric acid. For diazotization, the amine is dissolved in sulphuric acid or glacial acetic acid and 1-equivalent of nitrosyl sulphuric acid is added to it. As before, diazotization is carried out at very low temperature of (0-5°c).

5) DIAZOTIZATION OF HYDROXYAMINES:- Hydroxyamines such as aminophenols and aminonaphthols are readily oxidized by nitrous acid to the corresponding quinones.

Sulhpuric acids derived from such 1:2 amino hydroxy compounds are mostly used as diazo components in the manufacture of metal azo complex dyes and special procedures are used.

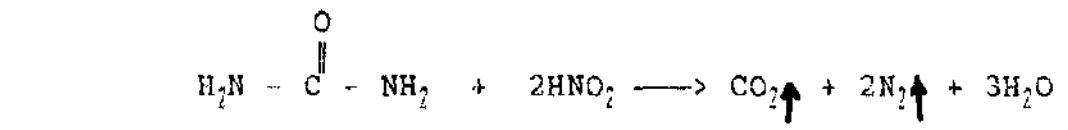
The hydroxylamine is suspended in water, copper sulphate solution is added, then finally $NaNO_2$ is added. Mineral acids are not used. Usually, diazotization takes place at higher temperatures for example 20^0c.

6) DIAZOTIZATION OF DIAMINES:- Attempts to prepare a diazo or tetrazo derivative of o-phenylenediamine result in ring closure with formation of benztriazine which does not couple with m-Phenylenediamine can be diazotized, but strongly acid conditions are essential if coupling with undamaged m-m-phenylenediamine is to be avoided.

Benzidine derivatives such as dichlorobenzidines, toluidines, etc can be smoothly tetrazolized; the products are stable in solution. Tetrazobenzidine can be made to couple twice, i.e. with formation of a diazo compound with the same or different coupling components. The second coupling proceeds less readily than the first, a consequence of the electron - supplying properties of the azo group formed in the first coupling, the effect being to reduce the positive charge on the second diazo group and thus to weaken its electrophilic character.

SUMMARY:- During diazotizations, acids are used (i) - to dissolve the amine (ii) - to generate the diazotizing species (iii) - to protonate the amine and thus prevent self coupling.

Excess nitrous acid causes decomposition of the diazonium ion ($RN-N^+$). Therefore, the end of the reaction is checked with starch iodide paper (blue-black coloration results). Any excess nitrous acid is destroyed with urea.



Generally, during diazotization, low temperatures (0-5°c) are used to keep the nitrous gases dissolved and to prevent decomposition of the diazonium ion.

1.6.5 DIAZO COUPLING

As earlier mentioned, practically all azo dyes are produced from diazo compounds and coupling components by means of the azo coupling reaction.

The diazonium ions formed during diazotization gives rise to azo compounds in a subsequent electrophilic aromatic substitution of a nucleophilic substrate (coupling component) in azo coupling. As diazonium ions are relatively weak electrophilic reagents, only aromatic compounds that carry electron donor substituents (OH, NH_2, NHR, etc) can normally be used as coupling components.

In carrying out azo coupling it is therefore, necessary to take into account, not only these pre-equilibria of the diazo compounds, but also those of the coupling components. Due to the fact that the reactivity of the nucleophilic substrate increases with rising basicity, the phenolate ion ($Ar-O^-$) and the free amine ($Ar-NH_2$) react more readily as coupling components than free phenol (Ar-OH) and the ammonium ion ($Ar-NH_3^+$)[1].

The positions where coupling will occur are those in which there is increased electron density. Generally at carbon atoms in aromatic systems or heterocyclic systems aromatic in character, and in some cases, at activated carbon atoms occurring in aliphatic chain as in acetoacetanilide. This is due to the fact that diazo coupling is an electrophilic substitution by a diazonium ion.

Coupling reaction may be represented as follows:-

$$Ar\ N_2^+X^- + HR \longrightarrow Ar\ N - NR + HX$$

where R = Alkyl or Aryl group.

In coupling there are two competing reactions

i) $R - N_2^+X^- + HR \longrightarrow R - N = N - R + HX$

ii) $R - N_2^+X^- + HOH \longrightarrow R - OH + N_2 + HX$

Therefore, coupling reaction must be carried out in a suitable medium in which the equilibria of the diazo and the coupling components lie as far as possible towards the diazonium ion, the phenolate anion or the free amine, depending on whether coupling is performed with phenol, naphthol or with aromatic amine. This results in an optimum coupling pH region for each combination of diazo and coupling components. This region lies, approximately between pH4 and pH5 with aromatic amines as coupling components and pH9 for phenols and naphthols.

High temperatures exert an unfavourable influence in most cases on coupling reactions. This is because the diazo decomposition reaction have larger activation energies and

therefore, a larger temperature gradient than the coupling reactions.

With some azo couplings, the addition of common salt before coupling gives a higher yield. This can be attributed to the different dependence of the reaction rate of coupling and diazo decomposition on ionic strength.

1.6.6 COUPLING COMPONENTS

There are essentially three types of coupling components.

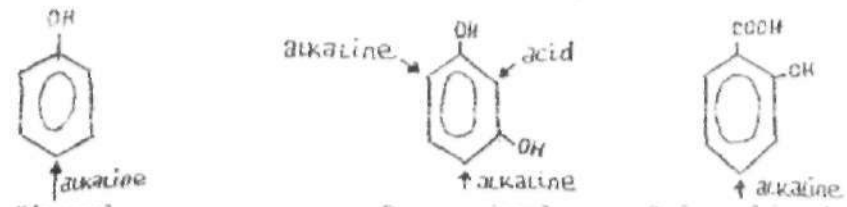
I) Hydroxy derivatives (phenols & naphthols).

II) Amines.

III) Active methylene compounds.

I) HYDROXY DERIVATIVES

a) Phenol and its derivatives, e.g.

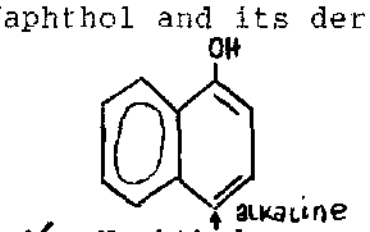


Phenol Resorcinol Salicylic Acid

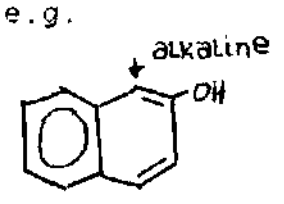
Phenols couple under alkaline condition principally in the 4-position. However for resorcinol, coupling occurs first at 4-position under alkaline condition and then the second coupling is done at position 2 or 6 according to pH i.e. acidic at position 2 and alkaline at position 6.

Salicylic acid is widely used as coupling component under alkaline condition.

b) Naphthol and its derivatives, e.g.



α- Naphthol

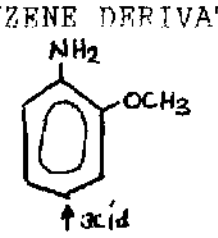


β - Naphthol

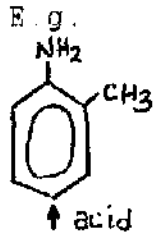
β - Naphthol is more widely used as coupling component than α- Naphthol. ...ver, both of them couple under alkaline condition as indicated by the arrow(s). β - Naphthol couples much more readily and under less alkaline condition.

II) **AMINES**:- The two types of amines encountered as coupling components are the benzene derivatives and the naphthalene derivatives.

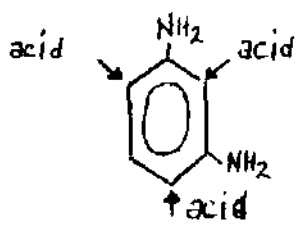
a) BENZENE DERIVATIVES. E.g.



Anisidine



O-Toluidine



m-phenylenediamine

As shown above, coupling takes place under acid conditions at the position(s) indicated by the arrow(s). In case of m-phenylenediamine an energetic diazo component ... be used for successful coupling.



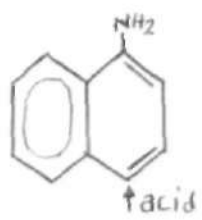
Weak diazonium cation
(less electrophilic)



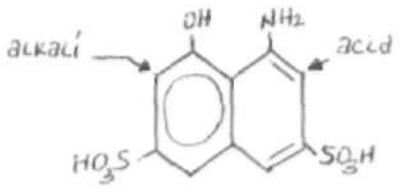
strong diazonium cation
(more electrophilic)
Energetic diazo.

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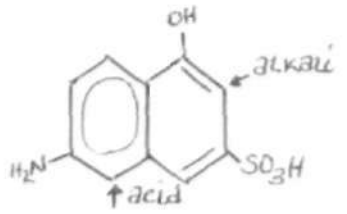
b) NAPHTHALENE DERIVATIVES.



1 - Naphthylamine



H - ACID



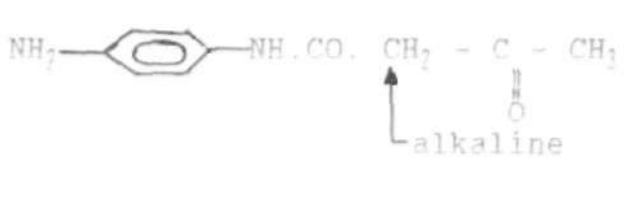
J - ACID

1-Naphtylamine is used as a diazo component as well as a coupling component under acid conditions or both.

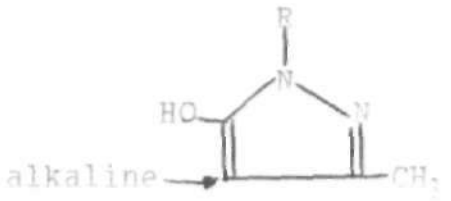
H-acid (1-Naphthol-8-amino-3,6-disulphonic acid) and J-acid (1-Naphthol-6-amino-3-sulphonic acid) both couple at positions indicated by the arrows first under acid conditions and second coupling under alkaline conditions.

III) <u>ACTIVE METHYLELENE COMPOUNDS</u>

An active methylene compound contains $-CH_2$ (methylene) group which is acidic. The acidic hydrogen atoms ionize on dissolving in NaOH to provide the coupling position. Typical example is shown below:-



Acetoacetanilide

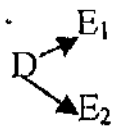


3-methyl-1-phenyl-5-pyrazolone

Both are employed in the manufacture of direct dyes, acid dyes, and pigments.

1.6.7 SYNTHESIS OF DISAZO DYES

Dyes having two azo (-N=N-) groups in a molecule are produceded in three different ways.[15] i.e.

I) TYPE 

A few of these dyes are made from arlyenediamines as D – components. Usually a nitroarylamines is diazotized and coupled with E1, the nitro group is reduced, then the amines is diazotized and coupled with E2.[15]

(II) TYPE A ⟶ M ⟶ E

This is a fairly large group. The A-components are variously substituted anilines and Napthylamines.

Example of the middle component(M) include 2,5-xylidine and J –acid (6-animo-1-naphthol-3-sulphuric acid). There are several widely used end components (E) such as J-acid and 1-amino-8-naphthol-2,4-disulphonic acid (Chicago or 2S acid.) [15]

(III) TYPE A^1 ⟶ Z ⟵ A^2

The dyes of this group are not numerous but their importance is by no means negligible. They fall into two groups. The first consist of orange(s) and brown(s) dyes obtained from z-components such as m-phnylenediamine, m-phenylenediamine sulphuric acid or resorcinol. The A-components include anilines, naphthylamines, and their sulphonated derivatives.

The second group consist of dyes derived from symmetrical z components containing two aromatic residues linked by groups such as -NHCONH- or -NH-; some of these are obtained by phosgenation of amino azo compounds and often contain no auxochrome.

The coupling properties of sulphonated amino naphthols are of importance because some of these compounds are extensively used as coupling components for azo dyes of various kinds. In acid conditions coupling is directed by the amino group into an ortho or para position , but in alkaline medium the azo group enters in an ortho or para position with respect to the hydroxyl group. Sometimes disazo dyes can be obtained by coupling first one molecule of a diazonium compound in acid medium, then a second molecule in alkaline medium.[37]

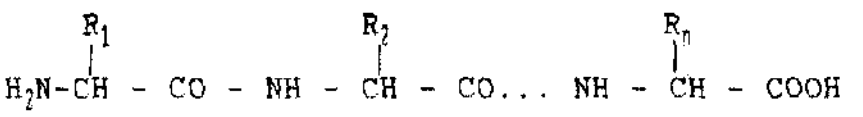
1.7 FIBRE STRUCTURE IN RELATION TO DYE MOLECULAR STRUCTURE

Textile fibres, whether natural or synthetic consist of polymer molecules as their fundamental units. The functional groups within the polymers retain their chemical properties and determine the type of dyestuff for which the fibre would have an affinity. Generally fibres having many polar functional groups (hydrophilic fibres) will have greater affinity for the ionic dyestuff, while those having very low polar groups or none at all (hydrophobic fibres) will have greater affinity for non-ionic dyestuff.

Crystallinity tends to impart hydrophobicity to fibres even having polar functional groups. This is due to the screening off of polar functional groups with possible intermolecular hydrogen bonds. Also, the close arrangement of polymer molecules leaves little or no space for dye molecules to penetrate into it from the dye bath.[43]

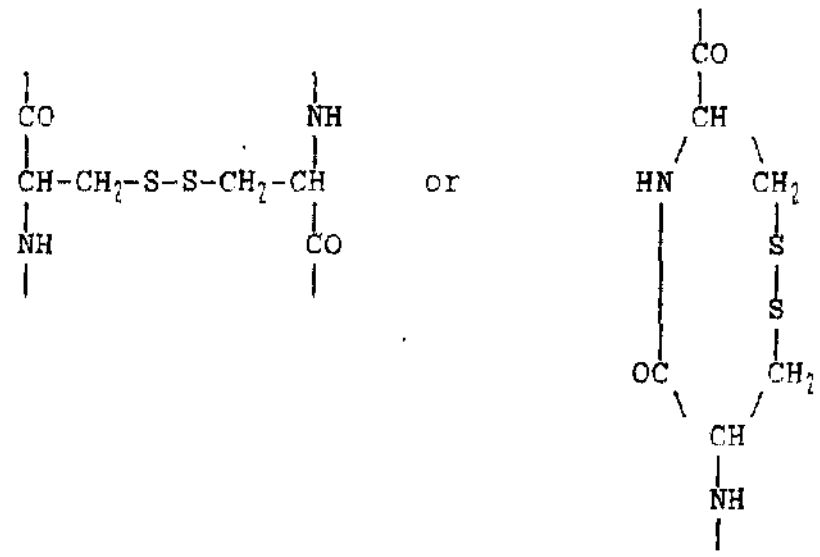
1.7.1 WOOL STRUCTURE AND PROPERTIES IN RELATION TO DYEING

Wool being a protein (keratin) is made of long polypeptide chains of amino acids as shown below:



Where the R are side chains or groups of amino acids which differ in size and chemical nature. These side groups are of importance to the chemical reactions of the fibre.

Purified wool consists of keratin whose elementary composition is nearly same for all kinds of wool, but the sulphur content varies within great limits. Cystine, the main sulphur containing amino acid in wool plays a major role, as two of the residues form a disulphide cross-link (cystine linkage) between neigbouring polypeptide chains or amino acid residues in the same chain. i.e.



As a result, considerable attractive forces exercise their action in the cross and longitudinal directions. Under the effect of these forces, active side chains strike to approach each other as close as possible by curving themselves and causing bending of the principal polypeptide chains.

All properties including fibrous (keratin and fibroin) proteins contain acid and basic groups in their composition. Owing to this, they can dissociate both as acid and base, thus acquiring the ability to combine both with bases and acids i.e. they are amphoteric. As such the basic groups (arginine, lysine and histidine residues) can attract acid (anionic) dyes, while the side chains of lysine and histidine residues are sites of covalent attachment of reactive dyes.

Wool is distinguished by its high hygroscopicity. It absorbs large amount of moisture, depending on humidity and temperature of the surrounding medium and hence is comfortable to wear.

Wool swelling due to moisture regain greatly enhances the penetration of dyes into the fibres. Some water soluble dyes e.g. acid dyes entre the fibres with ease without the aid of swelling agents.

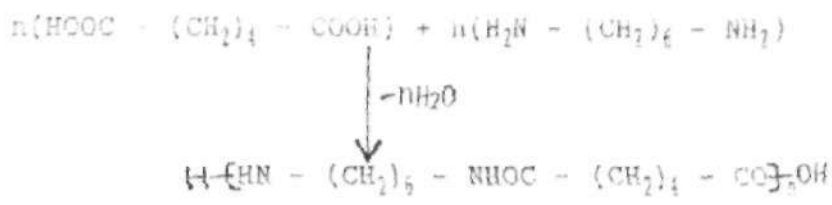
Fibres dried at high temperature (100-105°C) Loss their moisture thus becoming rigid and less strong. On repeated wetting, wool absorbs moisture again and its softness and strength are restored and its electrical conductivity becomes high.

Wool fibre is characterised by high extensibility and relatively low breaking strength. It is therefore, wrinkle resistant. Natural crimp or waviness of the fibres gives it bulk, enables it to trap air and so provides insulation and warmth.

1.7.2 NYLON STRUCTURE AND PROPERTIES IN RELATION TO DYEING

Nylon is the generic name for a group of polyamide fibres whose long polymer chains have the recurring amide (CONH) linkage predominant in the molecule.

The most common species of nylon are the nylon 6.6 produced by the condensation of adipic acid and hexamethylene diamine.



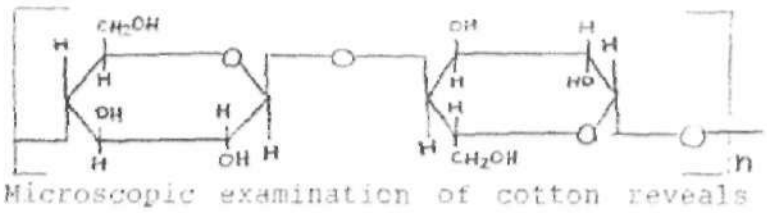
Nylon 6.6

Acid dyes fixation is possible on nylon due to the presence of amino ends groups. Depending on the proportion of amino end group (AEG) per kilogramme or polymer chain, a variety of nylon types are available, such as light dyeing nylon; - where some of the amino end groups have been converted to imines to reduce acid dye absorption; deep and ultra deep dyeing nylon where carboxylic acid end groups have been converted to amino end groups by the means of diamine to increase acid dye absorption. Basic dyeable nylon prepared by converting amino end groups to acidic groups e.g. sulphonic acid thus increasing its affinity for cationic dyestuff.[11]

Nylon is a semicrystalline fibre with amorphous region for the dye molecules to migrate into. However, effective sites of dye attachment are screened off from the dye molecules in crystalline region.[11]

1.7.3 COTTON STRUCTURE AND PROPERTIES IN RELATION TO DYEING

Cotton fibre belongs to the group of cellulosic fibres, which is composed of glucose molecules linked together.



Microscopic examination of cotton reveals that it is characterized by half-flat convolutions and it has a bean-shaped cross section.

Cotton is fairly strong with tenacity of 3-5g/denier. It stretches only to a small extent, 5-10%. It is relatively inelastic and rigid. It has a moisture regain of 8.5% and specific gravity of 1.54.[11]

Cotton is insoluble in water despite its hydrophilic nature but it swells in water. It is highly resistant to organic solvents like benzene, ether etc. It also has excellent resistance to alkalis. However, it is very susceptible to acid, especially to the mineral acids.

1.8 FIBRE - DYE ATTACHMENT

This mainly has to do with the strength of dye-fibre, dye-resin and dye-dye molecular bonds formed within the fabric. These bond strengths in turns depends on the nature of the fibre and the type of dye.

The nature of the fibre on which the dye molecule is present contributes greatly towards the colour fastness of the dyed fibres. This is due to the chemical and physical interaction between the dye molecule and fibre.

The nature of chemical bond and/or physical interaction between the dye molecule and the fibre is mainly responsible for the strength of the fibre - dye attachment.

Covalent bonds formed between reactive dyes and their substrate fibres have the strongest dye - fibre strength and unless under severe conditions or in the presence of water containing chlorine, these bonds are not easily broken.

Direct dyes employ hydrogen bonds (and Van der Waals forces where the molecule is planner) to hold these molecules on to the fibre substrate. These dye fibre bonds are easily broken as there is competition between the fibrous substrate and the liquid for the formation of hydrogen bonds with the dye molecules.

Acids and basic dyes employ electrostatic bonding, which involve transfer of electrons from one atom to another and is characterised by electrostatic attraction between ionic charges on the fibre molecule and the dye molecule. It is affected only by the local charge density effect.

Chemically, however, certain functional groups within the fibres could in the presence of agencies such as light, react with dye molecule in its excited state. Thus as the dye fades the fibre also loses some of its features e.g. phototendering of cotton by some vat dyes.[42]

Increased light fastness is observed when acid dyes are used in the colouring of anodized aluminium. This was supposedly due to the trapping of excited ion formed by the polar substrate which would result in the stabilization of the dye.[11]

1.9 COLOUR FASTNESS

The colour fastness of dyed or printed textiles is the measure of change in the depth of colour, hue and brightness observed when it undergoes exposure to agencies such as are encountered during further processing of the dyed fabrics as well as in use.

Such changes in depth of [illegible], hue or brightness may be as a result of one or more [illegible] following.[46]

a) The chemical breakdown of the colourant while still held within the fibre to give uncoloured or differently coloured compounds, which results from the interaction of dye molecule with either (i) chemical substances within the dye-fibre system, in the immediate surrounding, or (ii) photochemically

activated species within the dye-fibre system, or in the immediate surrounding.

b) Detachment of the colourant molecules from within the fibre i.e. without any chemical degradation of the colourant.

c) Changes in the physical and chemical structure of the fibre during processing or in use which in turn may affect (A & B) above.

d) Staining of undyed areas of the sample or adjacent materials occurs under conditions similar to those that facilitate dyeing e.g. temperature, pH and substantivity of the dye for the fibre.

Colour fastness properties of dyes may be improved by physically or chemically improving the properties of the dye - fibre attachment; for instance, inhibition of migration of the dye molecules within the fibre or cause the formation of less mobile, long or heavy molecular chains or complexes with the dye molecules within the fibre.

1.10 FACTORS AFFECTING FADING OF DYED TEXTILES

A- The photostability of the dye molecule is determined by the reactivities of the excited states.[57] In general, the chromophore nucleus is most important in determining the light fastness of a dye, but nuclear substituents may substantially alter the fastness one way or the other.

B- The dye concentration. The light fastness of a dyed fibre usually increase in fastness with increasing dye concentration. In many cases, this increase in fastness is caused by aggregation of dye molecules within the fibre.

C- The wavelength distribution of the incident radiation.[49] Not all absorbed wavelengths in the visible and ultraviolet are equally effective in initiating a fading process. It was shown that fugitive dyes are faded mainly by visible radiation, while dyes of high light fastness are faded mainly by violet and ultraviolet radiation.

D- The nature of the fibre. Three kinds of effects appear to be important: (i) The reactivity of a dye in an excited state with certain chemical groups within the fibre; (ii) The stabilization of a dye by the quenching of the excited state through the agency of some group within the fibre; and (iii) The permeability of the fibre to various components of the atmosphere that are capable of reaction with the dye in its excited state.

E- Composition of the atmosphere. The moisture content of the atmosphere is known to have a pronounced effect on the fading rates of certain dyes. Atmospheric contaminants such as sulphur dioxide, oxides of nitrogen and ozone are known to react with dyes in absence of light. However, it seems possible that such reactions are accelerated when the dye is in an electronically excited state.

1.11 AIM AND LIMITATIONS OF THE PRESENT WORK

The main concern of this work is the synthesis of different disazo dyes particularly the type $A^1 \longrightarrow Z \longleftarrow A^2$

Attempts were also made to apply the synthesized dyes to wool, nylon and cotton using the normal methods of dyeing.

Some characteristics of the synthesized dyes will also be determined.

CHAPTER TWO

EXPERIMENTAL

2.1 MATERIALS AND REAGENTS

2.1.1 PRIMARIES FOR DYE PREPARATION i.e PRIMARY AMINES

1. Aniline
2. 2, 5 - Dimethoxyaniline.
3. Sulphanilic acid.
4. 4 - Nitro aniline.
5. 4 - Methylsulphonyl - 2 - chloroaniline.

2.1.2 COUPLING COMPONENTS

1. 1 - Naphthol - 8 - amino - 3, 6 - disulphonic acid.
2. 1 - Naphthol - 6 - amino - 3 - sulphonic acid.
3. Chromotropic acid.

2.1.3 OTHER REAGENTS

1. Concentrated hydrochloric acid.
2. Sodium nitrite.
3. Acetic anhydride .
4. Sodium hydroxide pellets.
5. Sodium carbonate.
6. Dimethyl formaldehyde (DMF)
7. Dry acetone.
8. Ice block
9. Distilled water.
10. Chloroform.
11. Ethanol.
12. Hexane fraction.

2.14 MATERIALS

1. Wool fabric (Woven)
2. Nylon fabric (Woven)
3. Cotton fabric (Woven)
4. Filter Paper.
5. Starch iodide Paper.

2.2 APPARATUS AND EQUIPMENT

1. Heating Mantle.
2. 3 - necked flask (250 ml)
3. Mechanical stirrer.
4. Regulator.
5. Mettler weighing balance.
6. 100ml measuring cylinder.
7. Watch glass.
8. 250mls beakers.
9. Spatula.
10. Glass rod.
11. Funnels.
12. Electric Oven.
13. 100ml volumetric flasks.
14. Thermometer.
15. Uv spectrophotometer.
16. SP800B mini spectrophotometer.
17. Dyeing master machine.
18. Linitest machine.
19. Martin Dale wear & abrasion tester.

2.3 SYNTHESIS OF INTERMEDIATES AND DYES

2.3.1 ACETYLATION OF H-ACID & J - ACID

ACETYLATION OF H - ACID

7.5g (0.0235 moles) of H - acid was dissolved in 150cm³ of distilled water at 50°C containing 1.4g of soda ash in 250cm³ three - necked round - bottomed flask equipped with a mechanical stirrer, water condenser and a thermometer. With vigorous stirring, about 1.2g of acetic anhydride was added into the flask over a period of 15 minutes. This resulted in complete acetylation of the amino group in the H - acid. However, partial acetylation of the hydroxyl group also occurs.

To test for complete acetylation of the amino group, a sample of the reaction solution was dropped onto a filter paper, acidified with hydrochloric acid, treated with few drops of sodium nitrite solution and finally made alkaline with aqueous caustic soda. A red yellow coloration formed by the nitrosation indicate complete acetylation of the amino group [60].

After complete acetylation, 6.23g of soda ash was added into the reaction mixture with stirring at 90 - 95°C for 60 minutes under reflux to hydrolyse off the acetyl group in the oxygen atom.

This final treatment was necessary so as to prevent loss of starting materials and contamination of final dye due to decomposition products of the diazo compound. The resultant alkaline solution of N - acetyl H - acid was used directly in the coupling reaction for the production of some of the dyes in this work.

ACETYLATION OF J - ACID

Similar procedures as for H - acid above was carried out with J - acid to obtain the alkaline solution of N - acetyl - J - acid which was used directly in the coupling reaction for the production of some of the dyes in this work.

2.3.2 DYE PREPARATION

All the dyes were prepared using the procedures for preparing azo dyes. The required amount of primary amine was diazotized under suitable conditions of 0 - 5°C, followed by coupling with the required coupling component to give the dye.

A) PREPARATION OF DYES 1 & 8

0.0075 moles of the primary amine in each case was diazotized at 0 - 5°C using direct method of diazotization.

The diazo component produced was coupled with an equivalent mole of N - acetyl H - acid at 0 - 5°C in the presence of 2.5 molar equivalent of hydrochloric acid to give the monoazo dye.

B) PREPARATION OF DYES 2 & 9

Similar procedures were carried out as (A) above, followed by second coupling with another prepared equivalent amount of diazo component (as in A) at pH 10 - 12 using sodium hydroxide solution, to give a disazo dye.

C) PREPARATION OF DYES Nos 3 & 10

Similar procedures were carried out as (A) above, except that N - acetyl J - acid was used as the coupling component.

D) PREPARATION OF DYES Nos 4, 5 & 11

Similar procedures as in (B) above were carried out using N - acetyl J - acid as the coupling component.

E) PREPARATION OF DYES Nos 6 & 12

0.0075 mole of the primary amine in each case was diazotized at 0 - 5°C using direct method of diazotization.

The diazo component produced was coupled with an equivalent mole of chromotropic acid at 0 - 5°C, pH 9 - 10 using sodium hydroxide solution to control the pH.

F) PREPARATION OF DYES Nos 7 & 13

Similar procedures as (E) were followed, however, second coupling was carried out using another prepared equivalent amount of diazo component (as in E) at pH 9 - 11 using sodium hydroxide solution to give a disazo dye.

G) PREPARATION OF DYE No. 19

4 - methylsulphonyl - o - chloroaniline is sparingly soluble in dilute HCl, but very soluble in hot concentrated acid, therefore suspension method of diazotization was employed.

1.534g (0.0075 mole) of 4 - methylsulphonyl - 2 - chloroaniline was dissolved in 1.2 molar equivalent of concentrated hydrochloric acid (0.3ml) and then diazotized using suspension method.

The diazo compound produced was coupled with an equivalent mole of N - acetyl H - acid at 0 - 5°C in the presence of 1.5 molar equivalent of hydrochloric acid.

A monoazo dye was produced.

H) PREPARATION OF DYES Nos 20 & 23

Similar method of preparation as in (G) above was carried out using 4 - methylsulphonyl —o— chloroaniline for dye No 20 and paranitroaniline for dye No 23 to produce the diazo component.

In each case, however, second coupling followed with another prepared equivalent amount of diazo component (as stated above) at pH 10 - 12 using sodium hydroxide solution to give a disazo dye.

I) PREPARATION OF DYES No 21 & 24

Similar method of diazotization was carried out as (G) using 4 - methylsulphonyl —o— chloroaniline for dye No 21 and paranitroaniline for dye No 24.

However coupling was carried out using chromotropic acid as coupling component under alkaline condition using sodium hydroxide to control the pH at pH 10 - 12.

J) PREPARATION OF DYES Nos 22 & 25

Same procedure of dye preparation was employed as (I), followed by second diazo coupling with another prepared equivalent amount of diazo component under alkaline condition pH 10 - 12.

K) PREPARATION OF DYE No 14

Sulphanilic acid is insoluble in acid but soluble in alkaline, therefore, inverse method of diazotization was employed.

0.0075 mole (1.3g) of sulphanilic acid was dissolved in 2mls of 2% NaOH, and then diazotized using indirect method of diazotization.

Coupling was carried out as in (C) above.

L) PREPARATION OF DYE No 15

Similar procedure as (K) was carried out, followed by a second diazo coupling with another prepared equivalent amount of diazo component as in (D).

M) PREPARATION OF DYE No 16

Same procedure of diazotization was carried out as in (K), followed by diazo coupling as in (E) above.

N) PREPARATION OF DYE No 17

Same procedure of dye preparation was followed as (M). However, second diazo coupling was carried out as in (F).

In each of the practical methods used in the preparation of the dyes No 1 to No 25, the dye produced was salted out, filtered and dried at 50°C in an electric oven.

2.4 PURIFICATION OF THE DYES

The dyes were purified in each case by dissolving in minimum quantity of DMF, filtered to remove insoluble materials and other impurities. The filtrate was then precipitated by addition of dry acetone.[60] The precipitated dye was filtered, washed thoroughly with acetone and finally dried in an oven at 60°C.

2.5 MELTING POINT DETERMINATION

The melting points of the twenty five dyes synthesized were determined using the Gallenkamp melting point apparatus. The values obtained are shown in table 3.1.

2.6 SPECTRAL CHARACTERISTIC OF THE DYES

The peak of maximum absorption wavelength (λ max) for each dye was determined in distilled water using unicam SP 800 spectrophotometer.

473423

The effect of solvent polarity on the absorption maxima of the dyes was also investigated in ethanol and DMF solvent chosen because they are wider apart in polarity. Similarly the effect of acid on the absorption maxima of the dyes was studied.

Using the λmax obtained in distilled water for each dye, the absorbance was recorded for a known concentration (C) of each of the dyes. The cell used has a thickness (L) of 1cm. The molar extinction coefficient of each dye was calculated using the relationship;-

$$\text{Log } E = \frac{A}{CL}$$

E = Molar extinction coefficient
A = Optical density or absorbance
C = Dye concentration (moles/l)
L = Path length of the cell (1cm)

The calculated molar extinction coefficient were recorded in table 3.1

2.7 APPLICATION OF THE DYES ONTO THE FABRIC

Each of the dyes synthesized was applied onto woven wool, Nylon and cotton fabrics by exhaustion dyeing.

Dyeing was carried out in a "Dyeing master" to ensure efficient stirring, using unsealed tubes. The dye bath was prepared using a liquor ratio of 50:1

All dyeing were carried out using 3% (owf) depth of shade at the boil for 30 minutes.

A) APPLICATION OF THE DYES ON WOVEN WOOL FABRICS

Dyeing was carried out in a "dyeing master" using unsealed tubes. From the 1% stock solution of the dye, 3.00cm³ was added to the dyeing tube (enough to give 3% shade o.w.f). 3.00cm³ of 10% acetic acid (o.w.f) was then added to each tube to obtain the

required pH6 and the dye bath was made upto 50ml with distilled water. A 1g sample of wool fabric was wetted out in hot water for a minute and excess water squeezed out. The wetted fabric was introduced into each of tubes by means of the stirrer hooks and then into a thermostatically controlled water bath in the "dyeing master" machine. The temperature was raised over a period of 15 minutes to 100°C and dyeing was carried out at this temperature for 30 minutes. After dyeing, the fabric was removed, thoroughly rinsed in cold running water and dried at 60°C in an oven.

B) APPLICATION OF DYES ON WOVEN NYLON FABRICS

The procedure for the dyeing of nylon was the same as for wool. The only difference was that the dyes were applied to 0.5g of nylon fabric here.

C) APPLICATION OF DYES ON WOVEN COTTON FABRICS

The dyes were applied to cotton fabric under neutral condition.

The procedures in (A) above was exactly followed except that 3.00cm^3 of 10% sodium chloride (o.w.f) was added to each dyeing tube instead of acetic acid in order to make the dyeing under neutral condition. And 1g of woven cotton fabric was used in place of wool fabric.

Appendix 2a shows the fabric dyed.

2.8 WASH FASTNESS TEST

The washing fastness tests were carried out using a "Linitest" wash-well machine.

International Standard Organization (I.S.O) Nos 2 and 3 washing tests were carried out on the dyed samples which were then assessed to determine the extent of change of shade, and staining of adjacent fabric using the grey scale.

METHOD FOR I.S.O. 2 TEST

The dyed sample(s) were each sandwiched between an undyed bleached cotton fabric and undyed wool for and cotton samples, while nylon samples was sandwiched between undyed wool and undyed nylon fabric, to form a composite sample(s) and each composite sample was stitched on all sides.

Each composite sample (10cm x4cm) was treated with 5g/1 soap solution using a liquor ratio of 50:1 at 50oC fpr 45 minutes. Continuos agitation was provided using LINITEST machine. The composite samples were each opened out at the expiration of the treatment time, then rinsed thoroughly and dried.

The staining of the white materials and the extent of changes in colour of the dyed samples were noted. These effects were compared with the untreated and treated dycing and assessments were made with the grey scales.

Results are shown on table 3.2 and Appendix 2B.

METHOD FOR I.S.O 3 TEST

The dyed sample(s) were sandwiched as stated above to form similar composites as for ISO 2 test.

The composite sample was treated with 5g/1 soap solution and 2g/sodium carbonate using a liquor ratio of 50:1 at 60oC for 30 minutes. The procedure then continued as for ISO 2 test above.

Results are shown on table 3.3 and APPENDIX 2B.

2.9 LIGHT FASTNESS TEST

The standard method of testing light fastness was not used because the standard materials for the test were not available; rather alternative methods were employed. In the standard method, the dyed sample under test is exposed along side with standard dyed samples under the same conditions. The standard dyed samples are blues on wool fabric provided by ISO. The standard dyed samples are produced with different dyes and ranging from No 1 - 8. No1 indicate very low fastness, and No 8 indicate excellent fastness (very high light fastness). When the sample has faded sufficiently it is compared with the standard and the number of the standard that behaves in the same way as the corresponding sample under test gives the rating of the light fastness of the sample under test.

However, in this project, the test samples were exposed to (i) Artificial light using the "XENON" Tester which uses Arc Lamp, the test samples were exposed here for eight hours, and (ii) Day light for thirty - six hours. At the end of each of these treatments evaluation of the degree of change of colour on the test samples as compared to untreated dyed samples is carried out using the Grey scale for assessing change in colour. (NIS 26 & 27: 1973).

The results obtained are summarized in Table 3.3 and APPENDIX 2c.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

3.1 RESULTS

TABLE 3.1 CHARACTRISTICS OF THE SYNTHESIZED DYES

S/NO DYE NO	MOLECULAR WEIGHT	MELTING POINT °C	% YIELD	λ_{max} (nm)				MOLAR EXTINCTION COEF. ($Mol^{-1}cm^{-1}$)	COLOUR OF CRYSTAL
				DISTILLED WATER	ETHANOL	DMF	ACID		
1	482	72	22.1	520	515	546	523	$9.23X10^4$	BROWN
2	500	206	47.3	500	525	585	565	$3.12X10^4$	DARK BROWN
3	402	132	85.5	490	505	530	510	$4.02X10^4$	ORANGE
4	506	157	62.6	550	566	585	574	$3.25X10^4$	RED
5	551	63	20.0	550	555	575	585	$2.86X10^3$	BROWN
6	483	234	84.9	510	485	540	560	$3.70X10^4$	VIOLET
7	587	241	87.1	510	515	535	573	$3.56X10^3$	VIOLET
8	510	85	88.7	545	550	562	562	$5.23X10^3$	BLACK
9	642	274	19.8	560	550	565	565	$8.11X10^3$	BLACK

CHARACTERISTICS OF THE SYNTHESIZED DYES

DYE NO	MOLECULAR WEIGHT	MELTING POINT °C	% YIELD	λ_{max} (nm)				MOLAR EXTINCTION COEF/MOL^{-1} cm	COLOUR OF CRYSTAL
				DISTILLED WATER	ETHANOL	DMF	ACID		
10	430	170	89.0	510	535	560	528	1.19X10^4	BROWN
11	502	255	71.5	565	580	620	585	1.09X10^4	BLACK
12	511	116	18.0	485	-	-	-	5.51X10^3	ORANGE
13	643	197	21.0	500	495	512	565	1.57X10^4	BROWN
14	482	207	84.5	529	543	570	568	2.97X10^4	RED
15	666	194	73.9	464	480	510	507	2.66X10^3	MAROON
16	563	248	73.9	473	450	525	462	3.65X10^4	BLACK
17	747	247	78.4	505	490	550	497	2.76X10^4	MAROON
18	594.5	235	12.4	545	530	558	583	4.7X10^3	BLACK
19	811	126	17.7	560	540	555	585	1.06X10^4	BLACK
20	595.5	250	78.5	520	505	580	524	4.05X10^4	VIOLET
21	812	258	72.0	530	520	605	535	7.39X10^4	VIOLET
22	676	273	75.1	480	360	510	425	1.0X10^4	BLACK
23	528	215	17.1	520	-	-	-	7.29X10^4	RED
24	677	126	19.4	530	538	570	560	3.3X10^3	BLACK

TABLE 3.2 WASHING FASTNESS TEST RATING

DYE NO	I.S.O 2						I.S.O. 3					
	CHANGE IN SHADE			STAINING			CHANGE IN SHADE			STAINING		
	WOOL	NYLON	COTTON	WOOL	NYLON	COTTON	WOOL	NYLON	COTTON	WOOL	NYLON	COTTON
1	2	4	2-3	2-3	2	3-4	2	3-4	1-2	3	3	4
2	2-3	4	2-3	2-3	2-3	3-4	2	4	1	3-4	3-4	4
3	4	4-5	2-3	2-3	3	4	4	4-5	1-2	3	3	5
4	4	4-5	3	4	4-5	4	3-4	4-5	1	3-4	4	5
5	4-5	5	3	4-5	4-5	3-4	4	5	2	4-5	5	1-2
6	4	4-5	1	4	4-5	2-3	4	4-5	1	4-5	4-5	2-3
7	4-5	5	1	4	5	1-2	4	4-5	1	4	5	3-4
8	3	3-4	2-3	3	3-4	2	3	3-4	1-2	3-4	3-4	3-4
9	2-3	3	2-3	2	3-4	3	2-3	3	1-2	3-4	3-4	3
10	2-3	3	2-3	2	2-3	1-2	2-3	3	2	2-3	3	3
11	3-4	3	3	1-2	3	2	3	3	1-2	2	2-3	3-4
12	2	2	1-2	2	2-3	3	2	2	1	2-3	2-3	3-4
13	2	2-3	3	2-3	2-3	3-4	2	2	2	3	3	4-5
14	3	3-4	1	3-4	3-4	4	2-3	3-4	1	4	3-4	4-5
15	4-5	4-5	2	2	3-4	2-3	4-5	4	1-2	2	3-4	3-4
16	2	2-3	2	3	3-4	3	2	2	1	3-4	3-4	3-4
17	3	3-4	1	4	4-5	4	2-3	3-4	1	3-4	4-5	4-5
18	3	3-4	2	2	2-3	3	3	3	1-2	3	3	3-4
19	4-5	4	2	3	3	3	4	4	1	2	3-4	3
20	3	3	1	4	4-5	4-5	3	2-3	1	4-5	4-5	5
21	2-3	2-3	1	4-5	4	4-5	2-3	2-3	1	4-5	4-5	4-5
22	3-4	4	2	4	3	2-3	3	3	1	4	3	4
23	4	4	1	2-3	4	5	3	3-4	1	3	4-5	5
24	4-5	4	1-2	2-3	3-4	4	4-5	4	1	3	3-4	4-5

TABLE 3.3 LIGHT FASTNESS TEST RATING.

	ARTIFICIAL LIGHT 'XENON' ARC LAMP			DAY LIGHT		
DYE NO	WOOL	NYLON	COTTON	WOOL	NYLON	COTTON
1	6	7	6	7	7	6
2	6	7	6	7	7	6
3	6	7	6	7	7	6
4	7	7	6	7	7	7
5	5	6	6	6	7	6
6	7	7	3	7	7	5
7	6	6	3	6	6	6
8	7	7	6	7	7	7
9	6	6	6	7	7	6
10	6	7	6	7	7	7
11	7	7	7	7	7	7
12	6	7	7	6	7	6
13	7	7	5	7	7	4
14	6	7	6	6	6	6
15	6	7	6	7	7	6
16	7	7	5	7	7	6
17	7	7	7	7	7	7
18	6	6	6	7	7	7
19	6	7	6	7	7	6
20	6	7	6	6	7	6
21	6	7	3	6	7	5
22	6	7	5	7	7	6
23	6	7	6	7	7	6
24	7	7	6	7	7	7

3.2 DISCUSSION OF RESULT

VISIBLE ABSORPTION SPECTRA

The visible absorption spectra of the dyes were measured in distilled water, and their molar extinction coefficient were calculated. The results are shown in Table 3.1.

Dye 1 obtained by coupling aniline with H-acid absorbs at 520 nm. When the dye is coupled again with a molar equivalent of aniline to obtain a disazo dye 2, it absorbs at 536 nm indicating a bathochronmic shift of 16 nm. This can be attributed to the increase in conjugation of the dye molecule due to incorporation of additional aniline ring.

However, hypsochromic effect was obtained with dye 23 which was produced from coupling H-acid with 4-nitro aniline to give a disazo dye. The λ max of dye 23 went down by 56 nm when compared with that of 2, due to the electron withdrawing effect of the nitro group(s) para to the azo functional group(s) in dye 23.

When aniline is substituted with 2, 5-dimethoxyaniline a bathochromic shift results, due to the effect of the electron donating power of the methyl groups at positions 2, & 5 of the aniline ring. Dyes 8 & 9 compared to dyes 1 & 2 respectively.

Dyes 3 shows a hypsochromic effect of 30 nm as compared to dye 1. This could be attributed to the positioning of the azo groups (non-linear) in the dye 3 molecule or the effect of the change in the coupling component, in this case J-acid replacing H-acid. A similar effect occurs when chromotropic acid was used as the coupling component i.e dye 6.

Dyes 21 and 22 show a bathochromic shifts as compared to dyes 6 and 7 which gave a blue shift relative to dyes 12 and 13 and absorbs at higher wave length compared to 16 and 17 respectively; in each case comparing the monoazo dyes with the disazo dyes. These show the effect of chloring and methly sulphonyl groups as compared to the other electron donors on the simple aniline used in this work.

A hypsochromic shift of 65nm is obtained when a monoazo dye 14 of sulphanilic acid with J-acid is converted to the disazo dye 15. This surprising result may be as a result of the effect of linearity of the azo group(s), such that dye 15 lost its linearity (supposedly) as compared to dye 14, when the second coupling was carried out.

Generally speaking therefore, from table 3.1 it could be observed that the disazo dyes exhibit bathochromic effect as compared to the monoazo dyes. This result conforms with what was obtained by Brooker[8] in his work, the effect on conjugation on the absorption maxima of cyanine dyes. Qualitatively, as conjugation increases the ground electronic state of the molecule is lowered even further due to stabilization resulting from rapid increase in the number of charged structures. This makes the difference in energy of the excited electronic state from the ground electronic state' ΔE becomes progressively smaller and hence the bathochromic effect.

The molar extinction coefficient, a measure of the amount of light absorbed by a compound in solution, was calculated for each

dye. From the results in table 3.1 it could be seen that dyes possessing high molar extinction coefficient appear on the fabric brighter (dyes 1 - 7, & 21 - 22). This is as a result of the fact that they transmit more light in comparison to others and therefore have narrow absorption bands with sharp peaks as compared to others.

SALVATOCHROMISM

The influence of solvent polarity on the wavelength of maximum absorption of the dyes were investigated and the results obtained are shown in table 3.1, Most of the shifts in maximum absorption wavelengths observed were bathochromic for the generality of the dyes where measurement were done in solvents of higher polarity. The λ max values are shifted to longer wavelengths when the solvent is changed from ethanol to a more polar solvent dimethylformamide (DMF).

As shown in Table 3.1, dye 13 absorbs at 512 nm in DMF, 500 nm in distilled water and 495 nm in ethanol. Likewise, dye 22 shows a maximum absorption of 605 nm in DMF, 530 nm in distilled water and 520 in ethanol. Similar trends were obtained in most of the dyes.

Salvatochromism has been extensively discussed over the years[30]. The reports indicated that $\pi \longrightarrow \pi^*$ transition exhibit bathochromic effect when the polarity of the solvent is increased, while $n \longrightarrow \pi^*$ transition exhibit hypsochromic effect with increase in solvent polarity. This clearly shows that in the present study, the visible band is due to $\pi \longrightarrow \pi^*$ transition since a general positive salvatochromic effect was observed on increasing the polarity of the solvent.

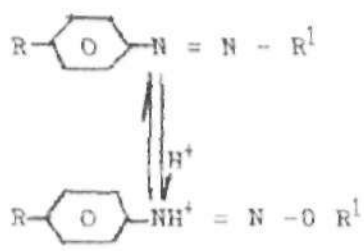
Solvatochromism is due to various solute solvent interactions in both the ground and excited states. $\pi \longrightarrow \pi^*$ transition[54] in the excited states of the molecule results in a higher electron density than in the ground state of the molecule. At the same time it is higher than in the excited state of the molecule caused by $n \longrightarrow \pi^*$ and $n - \sigma^*$ transitions. As a result of this, polar solvents stabilise $\pi \longrightarrow \pi^*$ excited states, thus lowering the energy required for its excitation. This is done by hydrogen bonding with hydrogen atoms of the solvent molecules[55]. With the $n \longrightarrow \pi^*$ or $\sigma \longrightarrow \sigma^*$ transitions the ground state is more likely to be stabilized by the hydroxyl groups of polar solvents. Thus a greater amount of electro magnetic energy would be needed to achieve the transition[56] i.e. $n \longrightarrow \pi^*$, $n \longrightarrow \sigma^*$.

HALOCHROMISM

Some of the dyes exhibited change of colour on addition of few drops of acetic acid to their dye bath as compared to their neutral aqueous solution. E.g Dye 3 changed colour from orange to violet Dye 12 changed colour in water from yellow to violet both upon addition of 10% acetic acid in the process of preparing their dye baths. It became necessary therefore to investigate the effect of acid on the visible absorption band (halochromism) of all the dyes. The results obtained are shown in table 3.1. The halochromism of the dyes synthesized were studied in ethanol as solvent and the shifts of the absorption maxima on acidification with hydrochloric acid obtained.

In all the cases, the protonated solutions were neutralized carefully with weak alkali (sodium trioxocarbonate iv) to ensure that the original spectra were completely restored thus confirming that decomposition of the dyes had not occurred during protonation.

The halochromism of p - aminoazobenzene has been the subject of prolonged controversy among chemists[57], but it is now believed that protonation of p - aminoazo benzene dyes occurs almost exclusively at the β - azo nitrogen atom in the azo linkage to form an azonium[58] tautomer leading to bathochromic shift. This azonium tautomer and the protonated form is in all respect different from the neutral azo compound. This is due to factors such as resonance stabilization of the resulting azonium cation[59].



As shown in table 3.1, most of the dyes under study exhibit pronounced positive halochromism, i.e shift of the absorption band to longer wave length on addition of acid.

However, dye 10 showed a negative halochromism of -7. In other words, the λmax of dye 10 drops by 7 nm when acid is added to its solution in ethanol. This may be attributed to the strong effect of the dimethyl groups on the p - aminoazo benzene ring of the dye that was protonated.

DEPTH OF COLOUR SHADE

The synthesized dyes were applied to wool, nylon and cotton fabrics, the depth of shades on each sample dyed was observed and compared, Appendix 2A.

Wool dyeings show medium to very deep shades with the synthesized dyes. All nylon dyeings have medium shades, while cotton dyeings show various shade from mere staining to deep shades as shown in table 3.5A.

TABLE 3.5A SHADES OF THE SYNTHESIZED DYES ON WOVEN WOOL FABRIC

COLOUR SHADE	DYE NUMBER
PALE	22
MEDIUM	1, 2, 4, 5, 7, 15, 17, 21
DEEP	3, 6, 9, 11, 12, 16, 19, 23, 24
VERY DEEP	8, 10, 13, 14, 20, 25

TABLE 3.5B SHADES OF THE SYNTHESIZED DYES ON WOVEN NYLON FABRIC.

COLOUR SHADE	DYE NUMBER
MEDIUM	ALL 24 SYNTHESIZED DYES

TABLE 3.5C SHADES OF THE SYNTHESIZED DYES ON WOVEN COTTON FABRIC.

COLOUR SHADE	DYE NUMBER
STAIN (ONLY)	6, 7, 16
PALE	1, 4, 5, 12, 13, 17, 21, 22
MEDIUM	2, 3, 9, 14, 15, 19, 20, 23, 24, 25
DEEP	8, 11
VERY DEEP	10

The dyeings show that wool fabrics absorption of the dyes are much higher compared to nylon and cotton absorptions of the dyes. The superiority of the wool fibre substantivity to acid azo dyes as compared to that of nylon fibre is evident from tables 3.5A & B. This is not unconnected to the amount of amorphous region in wool fibre as compared to nylon fibre. The higher crystallinity of nylon fibre and fewer dyeing sites (amine end groups) does not allow high penetration of the dye during the dyeing process when compared to the penetration of the dye into the more amorphous regions of wool fibre. However, the dye substantivity for nylon is also very good for all the dyes.

In both wool and nylon dyeings the colour(shades) of all the dyes are good indicating that the two fibres (wool & nylon) have good affinity for the dyes. The amino end groups present in both nylon and wool fibres react with the acid dyes as shown below.

$$\text{Dye} - SO_3Na + H_2N - \text{Fibre} \xrightarrow{H^+} \text{Dye} - SO_3^-H_3^+N - \text{Fibre} + Na^+ \text{ (in solution)}$$

The electrostatic attraction between positively charged ion of the fibre and negatively charged ion of the dye is responsible for the dye fibre attraction.

However, for cotton, the fibre - dye attachment is formed by hydrogen bonding and Vander Waals forces, as such, where these bonds are not strong enough to bind the dye to the fibre, the fabric appears only stained, but as the planarity and linearity of the dye improved and the dye weight increased, the substantivity of the dye for the fibre improved.

The competition for the hydrogen bonding between the fibre and water molecules for the dyes further worsened the poor substantivity of the fibre for the dye. This is clearly shown on cotton dyeings with dyes 6, 7 & 16.

Dyes 10 & 11 could be used as direct dyes on cotton as they give deep shades on the cotton fabrics. This may be attributed to planarity of the dye and low solubilizing sulphonic acid groups on the dye which reduces the competition between the fibre and water molecules for the dyes and therefore enhances the attraction between the fibre and the dye molecules.

LEVELLING PROPERTIES

The migration property of acid dyes on wool makes level dyeing readily attainable, particularly in dyes of low molecular weight. However, as the molecular weight increases, the movement of the dye molecules slows down and the electrostatic attraction between the charged ions of the dye and the fibre is over-taken by non-polar Van der Waals forces exerted between hydrophobic dye anions and hydrophobic regions of the wool fibre, their strength being proportional to the area of contact[30].

In this work, all the wool dyeings exhibit good levelling property. This is certainly due to the relative low molecular weight of the dyes.

However, the levelling properties on the nylon samples show variations. While some of the nylon dyeings exhibit very good levelling properties, others show serious unlevelness which arises from the appearance of barre' resulting from either[5] (a) PHYSICAL

VARIATION on the fibre which can result from several causes and effect of the ratio of the crystalline and amorphous regions in the fibre that can be attributed to several factors such as difference in draw ratio etc. Or (b) CHEMICAL VARIATIONs on the fibre which is brought about by differences in the amine end group content along the length of the nylon filaments or yarns, and the effect of the dyeing behaviours of those dyes which are attached to protonated (N^+H_3) amine groups such as acid dyes.

Acid dyes being anionic are sensitive to any chemical variation in the fibre. Thus dyes 1, 2, 3, 4, 5, 8, & 10 were unable to cover the irregularities (barre') present in the distribution of the amino end groups of the nylon sample. This might be as a result of the presence of acylamino group on the dye molecules which increases the dye-fibre affinity and hence lower the levelling property. However, introduction of the second azo group in the presence of alkali might have brought the decrease in dye-fibre affinities of dyes 9 & 11 resulting in well levelled nylon dyeings.

The addition of sulphonate groups in dyes 14 & 15 causes a decrease in affinity for the nylon, thus giving very good levelled dyeings.

All the dyes produced from chromotropic acid gave good levelling properties, which might be attributed to the absence of polar acylamino group on the dye molecules for low molecular weight dyes and the relative high molecular weight of the others.

The cotton dyeings showed no problem at all on levelness. This is as a result of the fact that the attachment bond between the substantive dye molecule and the cotton fibre is that of Van der Waals forces are possibly hydrogen bonding. And that the more linear or planner the dye molecule the better the affinity, therefore the dye molecules could easily be distributed evenly within the fibre.

FASTNESS PROPERTIES

A dye must be able to withstand treatments in manufacturing processes and normal usage when present in the fibre. Thus, it must be fast to wet treatments and light.

A - WASH FASTNESS PROPERTIES

The resistance of the dyeings to alkaline hydrolysis was investigated using I. S. O 2 & 3 washing procedure. The results obtained are summarised in table 3.2. High wash fastness values of dyes are observed generally in relation with: -

(a) Intermolecular aggregation of dye molecules possessing increasingly non-polar substituents[13].

(b) Polarisable auxochromes which induce fixation onto fibre by hydrogen bonds[13].

(c) Increased coplanarity of the substituents with the rings of the aromatic frame work of the dye. These induce high substantivity and thus high wash fastness.

(d) On the other hand factors that influence the rate of diffusion of the dye in the fibre affect wash fastness properties, thus low molecular weight of the dye molecule and incorporation of solubilizing groups onto the dye molecule enhances desorption out of the fibre when in liquid medium.

From table 3.2, it can be seen that the fastness test rating for ISO 3 procedure on wool dyeings with the synthesized dyes showed a fairly good result. Twelve out of the twenty five dyes gave wash fastness ratings on wool between 2 - 3 to 3 - 4; fastness rating of 4 to 4 - 5 were obtained from about eight dyes, six of which are disazo, while only five dyes gave ratings of 2 and below, only one of which is a disazo dye produced from aniline and H-acid, (table 3.5A). The disazo dye (dye 2) which gave low wash fastness rating must be due to low molecular weight and presence of up to two sulphonate groups per dye molecule which enhances the solubility of the dye in alkaline solution.

The effect of increase in molecular weight and length in favour of increase in dye-fibre substantivity is clearly indicated by the fact that six out of the eight dyes with high fastness rating are disazo dyes and four out of the five dyes with very low fastness rating are monoazo dyes (Table 3.6A).

Dyes 3 & 6 are monoazo dyes with high wool fibre affinity giving high fastness ratings, possibly due to their low solubility; dye 3 has only one sulphonate group per dye molecule, and dye 6 because of its hydrophobic nature.

Dyes 3, 4, 5, & 15 are derived from J-acid, and as a result of the fewer solubilizing groups on the dye molecules their desorption out of the wool fibre is lower comparably, hence giving high wash fastness properties; 50% of the dyes with the high fastness ratings are derived from J-acid.

The wash fastness ratings of the nylon dyeings range from 3 to 5, indicating good fastness properties, (tables 3.2 & 3.6B). Due to higher crystalline content of the nylon fibre, deep shades (as in wool fibre) were difficult to obtain; that is to say there is low dye absorption in nylon fibre as compared to wool fibre which possesses higher amorphous content. (Therefore in nylon dyeings there is little loose [unfixed] dye molecule within the fibre hence the wash fastness properties are superior as compared to wool).

However, the nylon dyeings obtained from dyes derived from chromotropic acid generally showed poor wash fastness properties particularly dyes 12, 13, 16, & 21.

The cotton dyeings showed very poor fastness properties for both ISO 2 & 3. Table 3.2 shows values of 2 and below wash fastness ratings of the dyes on cotton using ISO 3 procedure, indicating poor dye-fibre substantivity. Low molecular weight acid dyes have no affinity for cotton fibre due to its high rate of diffusion as a result of the dye geometry and dye size (small sizes) as well as the presence of solubilizing sulphonate groups. However, as the molecular weight, length and planarity of the dye increase the dye fibre affinity might increased and therefore dye-fibre attachment achieved by Van der Waals forces and hydrogen bonding giving improved fastness.

TABLE 3.6A WASH FASTNESS GRADING ISO 3 RESULT ON WOOL.

WASH FASTNESS RATING	DYE NUMBER
LOW (1 TO 2)	3, 4, 5, 6, 7, 15, 20, 25
MEDIUM (2 -3) TO 3 - 4)	8, 9, 10, 11, 14, 17, 19, 21, 22, 23, 24
HIGH (4 TO 5)	1, 2, 12, 13, 16

TABLE 3.6B WASH FASTNESS GRADING ISO 3 RESULT ON NYLON.

WASH FASTNESS RATING	DYE NUMBER
LOW (1 TO 2)	12, 13, 16
MEDIUM (2 - 3) TO(3 - 4)	1, 8, 9, 10, 11, 14, 17, 19, 21, 22, 23, 24
HIGH (4 TO 5)	2, 3, 4, 5, 6, 7, 15, 20, 25

TABLE 3.6C WASH FASTNESS GRADING ISO 3 RESULT ON COTTON.

WASH FASTNESS RATING	DYE NUMBER
LOW (1 TO 2)	ALL DYES i.e (No 1 TO No 24)

LIGHT FASTNESS TEST RATING

The result of the light fastness tests were summarised in Table 3.3. The results for both exposure to day light and artificial light from `Xenon' Arc Lamp showed that generally the nylon dyeings are more resistant to light as compared to the wool dyeings which in turn is better than cotton dyeings.

The fastness to light of dyed fibre depends on many factors, the most important of which are the inherent photostability of the dye chromophore and the way in which this stability is affected by the chemical nature of the substrate.

The effect of the light on the wool dyeings shows that the dyes derived from chromotropic acid have better photostability, possibly due to the absence of free amino group on the dye molecule. The dyes from H-acid and J-acid show very good light fastness properties (but generally lower than those dyes derived from chromotropic acid). This may not be unconnected with the fact that their free amino group were protected by acylation.

Introduction of benzoic acid to the fourth position (dye 5) lowers the photostability of the dye. This is because electron releasing groups lower light fastness rating due to the fact that they release electrons to the azo group which is basically the site of photochemical interaction and later destruction[11].

The nylon dyeing shows excellent light fastness properties for all the synthesized dyes. However, on cotton dyeings the light fastness properties vary considerably. Dyes 6, 7 & 22 showed the least light fastness rating of 3, on exposure to Arc Lamp, probably due to poor planarity of the dyes. However, Dyes 11, 12, 17, & 18 showed the best light fastness properties due to better planarity of the dyes.

CHAPTER FOUR

4.0 CONCLUSION AND RECOMMENDATION

4.1 CONCLUSION

The result of the spectral investigation show that increase in the number of azo groups in dye molecular structure affects the wavelengths of maximum absorption (λmax) of the dye and in most cases causes a shift to a higher wavelength of absorption.

Dyeings obtained using the disazo dyes generally show deeper shades as compared to those obtained using the corresponding monoazo dyes.

Washing fastness tests carried out shows that all the dyes have excellent washing fastness on nylon, relatively good washing fastness on wool, but poor washing fastness on cotton. In most cases the disazo dyes showed improved washing fastness compared to their corresponding monoazo dyes.

Light fastness property was generally excellent on the wool, nylon and cotton for all the synthesized dyes.

However, dye penetration and absorption into the fibre are better for the monoazo dyes as compared to their corresponding disazo dyes particularly for the higher molecular weight dyes.

4.2 RECOMMENDATION

A lot of work has been done on monoazo dyes, however little is being done on disazo and other polyazo dyes. Therefore, there is the need to give some attention particularly to disazo dyes.

In the present work, some characteristics of some disazo dyes were investigated, but more effort should be put to investigate more characteristics and parameters, possibly compared with monoazo dyes derived from similar raw materials and intermediates.

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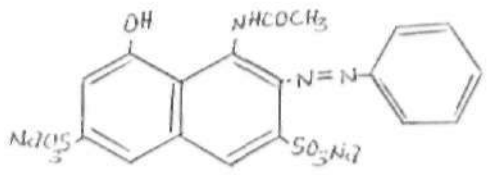
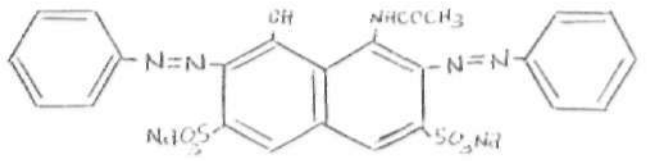
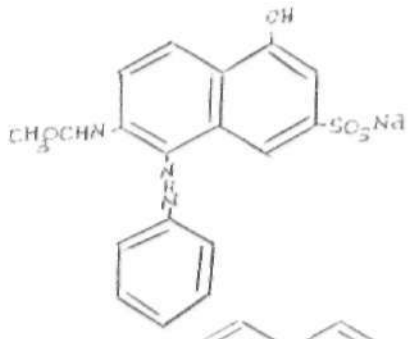
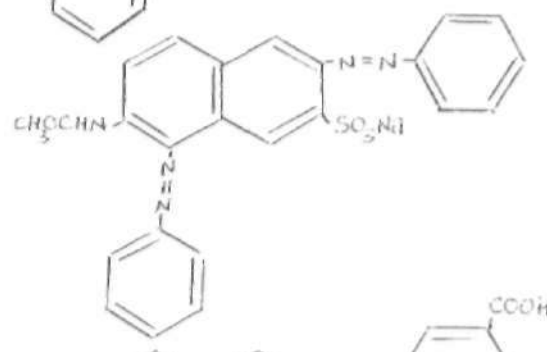
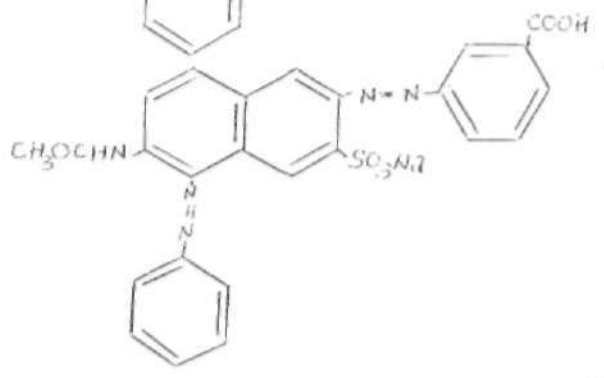
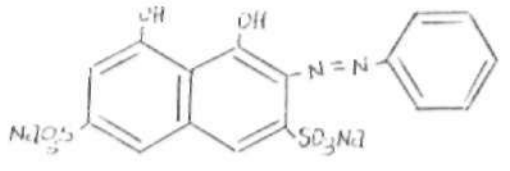
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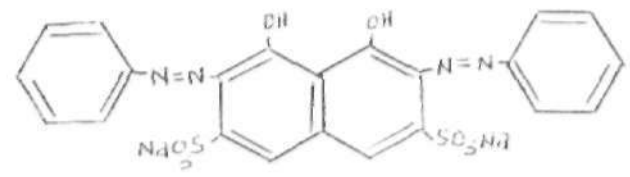
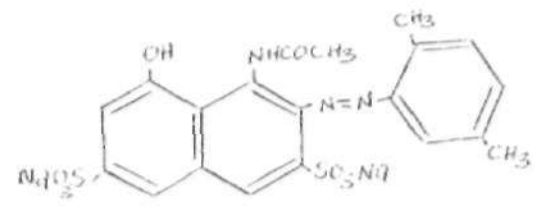
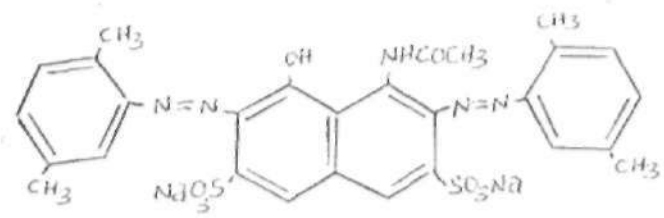
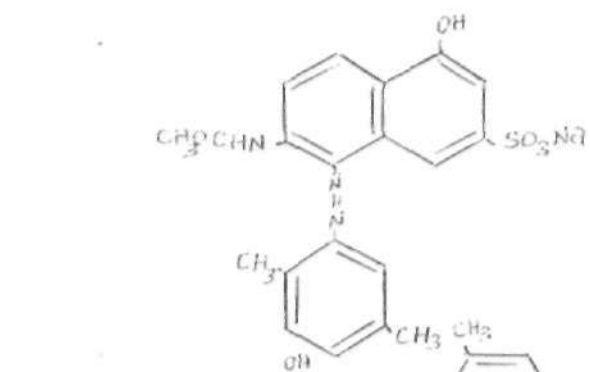
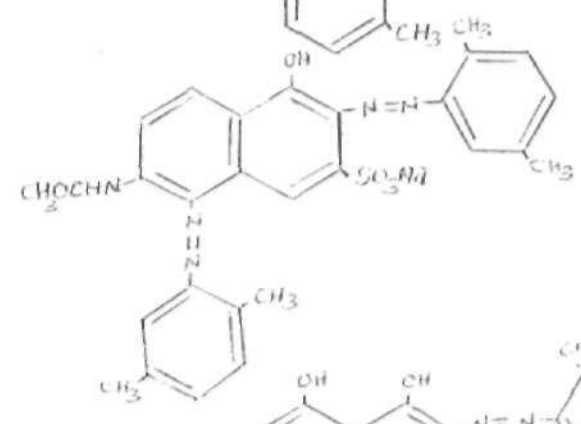
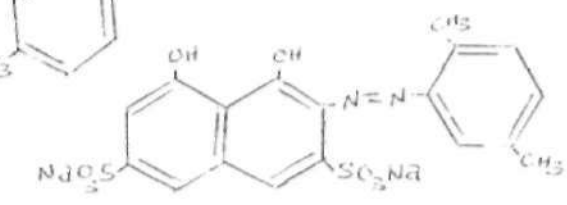
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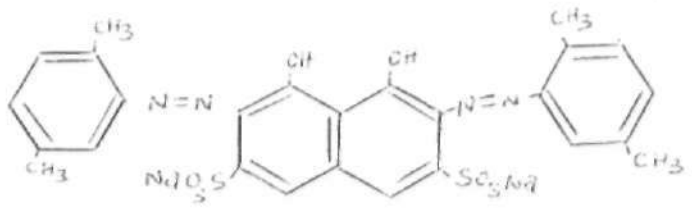
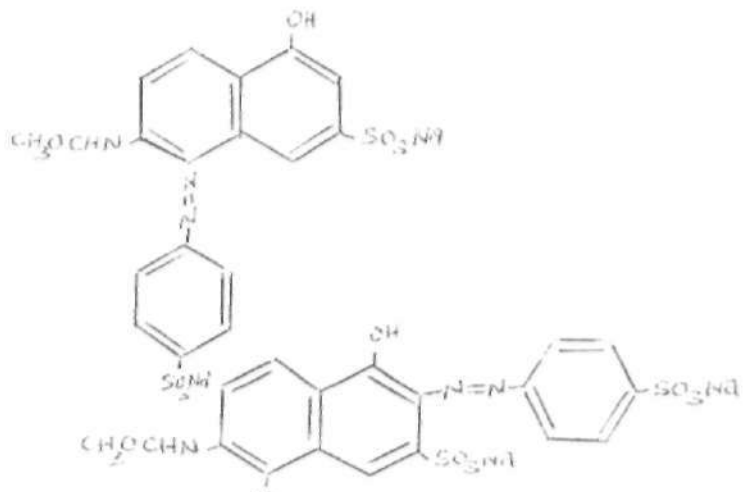
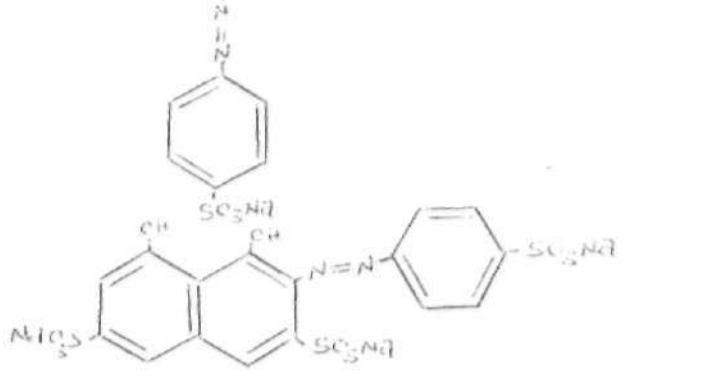
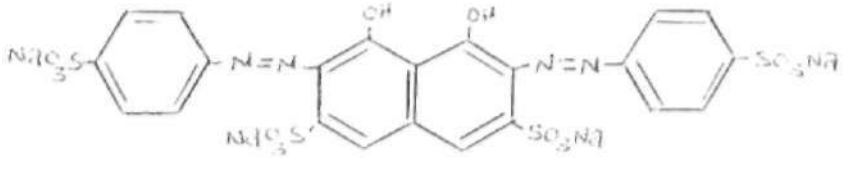
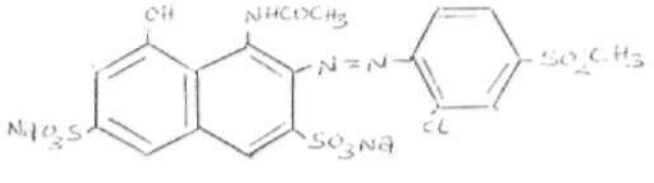
APPENDIX 1 DYE STRUCTURE.

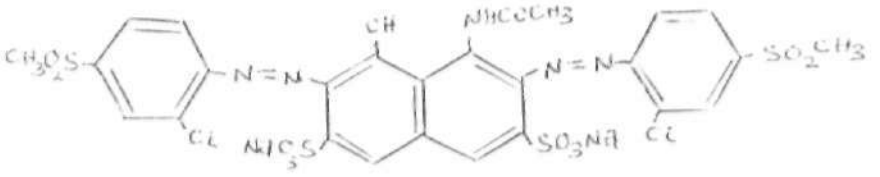
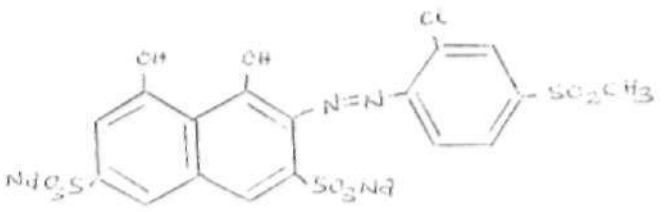
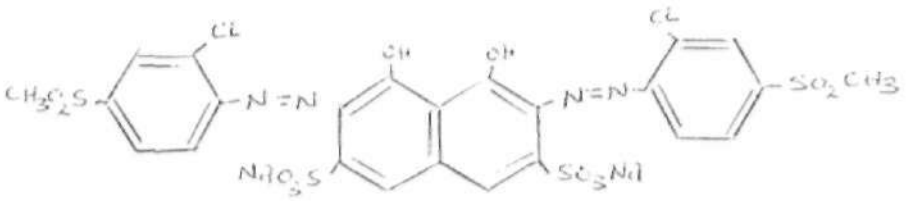
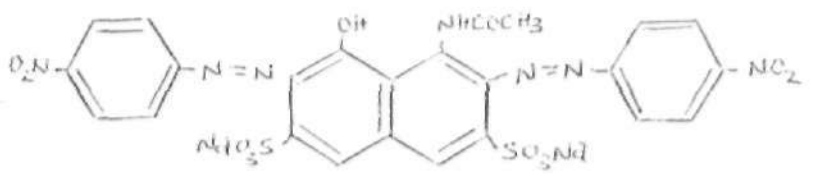
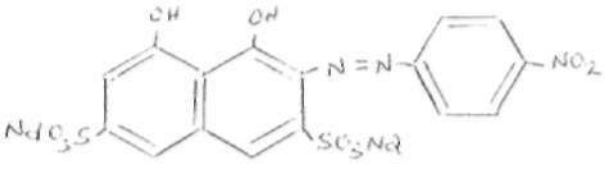
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APPENDIX 1 DYE STRUCTURE

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APPENDIX 1 DYE STRUCTURE

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