CHAPTER -1

HETEROCYCLIC DISPERSE AZO DYES - AN OVERVIEW

Preamble

From the earliest of times, people admired the beautiful natural colors of the plants and minerals, and used to enhance human appearance through color. To do so, they painted their bodies with various natural dyes like blue and purple color from indigo and woad plant, red dye from the cochineal bug. As the time went on, natural dyes were used more and more as cosmetics for hair, lips and cheeks. Then in the latter part of the nineteenth century, natural dyes were used to make foods and wine more attractive by using vegetable extracts of beet, carrot, turmeric etc. But the greatest use for natural dyes occurred when the art of weaving developed. Cloth dyed with alizarin a plant antharaquinone dye had been found in Egyptian tombs dating 6000 years ago. Tyrian purple was the most expensive and rare dye of the anticient world in the Eastern Roman Empire.¹ The first synthetic dye, Mauvine was discovered by Perkin in 1856 in UK and led to the many investigations of derivatives of coal-tar as potential coloring matters. In quick succession a number of other synthetic dyes appeared on the market and the natural dyestuff industry was doomed and at end of this century, the situation has changed dramatically to synthetic dyes. Natural dyes were replaced by synthetic dyes due to many reasons such as they are not many times economical and environmentally friendly and logistical to color the world’s textiles.

The history and growth of the dyes industry is inextricably related to that of the textile industry. The early dyes industry saw the discovery of the principal dye chromogens. Apart from the few notable exceptions, all the dye classes used today were discovered in nineteenth century.² The introduction of synthetic fibers, nylon, polyester and polyacrylonitrile during 1930 to 1950 produced the next significant challenge particular to synthetic dyes. Of these two most important fibers are cotton the largest and polyester. Consequently the manufacturers focused their efforts on producing dyes for these fibers and accelerated further research in synthetic dyes.

In this context, the last three decades of the dyestuff research trends have been focused on improved cost effectiveness and increased technical excellence in terms of
Chapter 1

brightness, high tinctorial strength and high fastness properties. This aim has been realized by replacing tinctorially weak anthraquinone dyes, with the tinctorially stronger dyes such as triphenodioxazines 1, polycyclic aromatic carbonyl azo dyes 2 and benzodifurannones 3 heterocyclic disperse azo dyes (4-6). 3

Today hetaryl disperse azo dyes are all-pervasive, either as chromophores (in phthalocyanine pigments) or functional components in fiber reactive dyes. 4 In disperse dye chemistry a number of heterocycles have been used as heteroaromatic diazo or coupling components. Consequently numerous heterocyclic dyes are now marketed to produce a full range of disperse dyestuff using hetero aromatic amines 5. In addition, these dyes have also been used in functional dyes applications, reprographic technology, photodynamic therapy and lasers since the commercialization of hetarylazo dye. 6-9 Many general reviews of synthesis, properties and applications of heterocyclic disperse azo dyes are appeared in the literature. 5, 10-14 However there has been a considerable number of industrially produced heterocyclic azo dyes remain undisclosed indicated in the patent literature and relative little information was available regarding their characteristic. Further the literature reports in the last decade have shown considerable growth in the research published pertains to the synthesis, properties and application of hetarylazo dyes.
Many hetarylazo dyes of technical interest for application to textiles are synthesized from hetarylamino diazonium components consisting of two or more nitrogen hetero atoms and are fused to another aromatic ring for examples amino imidazoles, pyrazoles, triazole, imidazole, pyrazoline, thiazole, thiazine, oxazine benzothiazole and thiophene etc.\textsuperscript{14-17} However few reports is available which pertaining to disperse azo dyes synthesized from pyrimidine heterocyclic analogues containing two nitrogen hetero atoms, as diazo components. Therefore it is an objective of this work to investigate the application of pyrimidine derivatives, as diazonium components in synthesis of heterocyclic disperse disazo dyes. Further to synthesize the disperse dyes of improved substantivity and water solubility Mannich bases derivatives of dihydropyrimidinone (DHPMs) with p-phenylenediamine and formaldehyde have been synthesized and used as diazonium components. Disperse azo dye formation based on these simple Mannich base compounds in an area which has not been developed except in a few patents.\textsuperscript{3, 18-22} Hence the present work concerns the synthesis and characterization of new Mannich bases of DHPMs and its use as dye intermediates in synthesis of novel heterocyclic disazo disperse dyes for dyeing polyester and nylon fabrics.

In addition to this, the other important of aspect work of environmental research has been planned regarding removal of synthetic dyes from water by using chemically modified polystyrene-DVB cation exchange resins adsorbents discussed as mentioned in the following. Water pollution control currently is one of the major thrust areas of scientific research since many industries such as, textiles papers, plastics use dyes in order to color their products and consume substantial volume of water in textile dyeing generating a considerable amount of colored waste water. Although, the growing impact of environmental protection on industrial development promotes the development of eco-friendly techniques, reduced consumption of fresh water and lower out-put of waste-water, the release of significant amount of synthetic dyes to the environment causes public concern, legislation problems and are a serious challenge to environmental scientists.\textsuperscript{23-25} In this context, color removal in particular, has recently become an area of major interest as indicated by the multitude of research reports and reviews regarding various treatment methodologies and emerging technologies and their advantages and disadvantages.\textsuperscript{26, 27} A wide range of methods
has been developed for the removal of synthetic dyes from waters can be classified into three main groups as physical, chemical and biological methods. The technologies involve adsorption on inorganic or organic materials, decolorization by photo catalysis and or by oxidation processes, microbiological or enzymatic decomposition etc. Among these methods, adsorption has been found to be an efficient and economic method for removal of dyes, pigments and other colorants and also control the biological oxygen demand since proper design of adsorption process will produce high quality treated effluent. Review of literature reveals numerous studies of utilization of different sorbents. But of these, most studies are based on employing activated carbon. The high cost of activated carbon sometimes makes its use limited and therefore efforts have been made to search for alternative materials which are relatively inexpensive and of reasonable adsorptive efficiency. In this context, the application of ion exchange resins has emerged as one of the significant polymeric material of industrial interest, in softening of drinking water, removal of toxic pollutants from the water in environment waste water treatment and bimolecular separation. Commercially available styrene-DVB cross-linked cation exchange resins with sulfonic acid groups are preferred for treatment of water contaminated with colorants or synthetic dyes. Recent developments in this field of application of cation exchange resins have used commercial styrene-DVB copolymer with reactive organic monomers such L-valine, amino pyridine, β-diketenes, dipyridylamine glycine containg acidic or basic groups. Consequently, the specific research objectives are to examine the application of a new generation material referred to as chemically modified sulfonic acid anchored chloromethylated polystyrene-DVB cation exchangers as an adsorbent in removal of synthetic dyes such as reactive dyes, acid dyes, direct dyes, cationic and basic dye. It is planned to study systematically the applications of chemically modified chloromethylated poly styrene-DVB cation exchangers with –SO₃H as adsorbents in removers of various synthetic dyes. The influence of phase contact time, cation exchanger dosage, solution pH, initial dye concentration was studied by the batch method. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. The kinetic data obtained at different concentrations. The research work conducted on these two aspects of synthetic dyes has been described in part I and part II of the present thesis entitled
“STUDIES ON SYNTHESIS AND CHARACTERIZATION OF DISPERSE DISAZO DYES AND NOVEL ADSORBENTS FOR REMOVAL OF SYNTHETIC DYES” As the research work presented in part I of the thesis relates to synthesis, properties, application of disperse azo dyes. It would be more reasonable to give brief description regarding their chemistry, dyeing applications and particularly polyester and nylon.

1.1 Disperse Azo Dyes - An Overview

1.1.1 Introduction

Dyestuff materials impart color to the textiles because of their ability to absorb electromagnetic radiation in the wavelengths visible to the human eye (400-700 nm). Therefore the dyestuff molecular construction is concerned with the synthesis of organic compounds that can selectively absorb visible electromagnetic radiation and have affinity for the specified fiber and balancing these requirements to achieve optimum performance. To be colored the dyestuff molecule must contain unsaturated chromophore groups likeazo, nitro, nitroso, carbonyl etc. In addition, the dye molecule can contain auxochromes, groups that enhance the chromophore effect on color. Typical auxochromes are amino, alkyl amino, hydroxyl, sulfonic and carboxyl groups. The discussion of different aspects of dyes and pigments (natural and synthetic) regarding chemistry, chemical structure, classification, dyeing properties, applications and their manufacturing and dyeing processes has been found in a number of literature reviews, encyclopedia, textbooks and journals etc. 4, 35-39

A colored substance to be considered as dye, if it must satisfied the requirements of substantivity for a textile, exhaust from aqueous solution into the fiber with high rate and provide high exhaustion, a uniform level dyeing and good fastness properties for the particular end use of the textile. The process of dyeing is therefore a combination of dyeing chemistry, application technology, economics, environmental concerns and customer needs. Recently heterocyclic based disperse dyes have gained importance and constitute the first example of the successful textile commercial exploitation of heterocyclic amines as the diazonium component in the production of yellow-red dyes. They have also found a new application as functional dyes which are ultra violet and infrared active molecules for various high technology applications.
The nomenclature of dyes is described either on the basis of chemical structure or color index system or commercial trade name. The classification of dyes based on chemical composition is more useful to dye chemist and dye technologist. Accordingly the dyes are classified as the azo, nitro, nitroso groups, phthalocyanine, imidazole, anthraquinone nucleus and heterocyclic ring system such as triazole, imidazoles, pyrazoline, thiazole, thiazine, oxazine etc structural units and named as azo dyes, nitro dyes, anthraquinone dyes etc shown in Table 1.1. The chemical constitution determines the properties of dye such as suitability for dyeing a specific substrate and the fastness properties of dyeing produced by applying the dye to substrate.

Application classification of dyes is more useful to the dyer. The textile industry is however interested in the dyeing properties of dyes rather than their chemical constitution. Therefore dye manufacturers market their products under names based on usage such as acid, basic, direct, disperse, reactive dyes etc. shown in Table 1.2. The principal system adopted for this classification is Color Index (CI) system which indicates dyeing class, the shade and sequential number and sometimes the other characteristics. On the otherhand commercial names of dyes are usually made up of three parts assigning trade name, color and code. Although the first two systems of subdivision of dyes overlap with each other, the chemical method is important from a chemistry viewpoint, whereas dyeing method is important from an industrial view point.

Of all classes of dyestuff, azo dyes have attained the widest range of usage due to the ease with which an extraordinary number of combinations can be generated by varying the diazo and coupling components, relatively simple manufacturing processes and provide a very wide color gamut of high color strength. The relative ease and economy of preparation of azo dyes by the classic diazotization of aromatic amines followed by coupling reaction with an electron-rich nucleophile have led to the synthesis of a large number of dyes. Therefore these dyes are the most numerous chemical group and cover all shades from yellow to navy blue with high extinction coefficients, $\varepsilon$ an efficiency to absorb specific wavelength (i.e. high tinctorial strength). They are used to color the vast majorities of apparel and household textiles as well as nontextile materials like paper, leather, foods, drugs, cosmetics and color
photography and constitute the largest group of synthetic dyes both in number and in commercial volume.\textsuperscript{42, 43}

Azo dyes are classified as to indicate the chief method of application into use as acid, basic (cationic), direct, disperse, mordant and reactive dyeing classes. From the chemistry viewpoint the disperse azo dyes are divided according to number of azo groups as monoazo, disazo, trisazo, tetrakis or polyazo dyes and as further subdivided into carbocyclic and heterocyclic (hetaryl) azo dyes according to the aromatic or heterocyclic radical present in a dye molecule. Benzene and naphthalene are by far the most important aromatic carbocycles used in the dyes industry. They are the backbone of the most commercial dye ranges providing yellow, red, blue and green colors for all the major substrates such as polyester, cellulose, nylon, polyacrylonitrile and leather. The carbocyclic azo dye classes are relatively economical to produce high color strength, good fastness properties but they lack brightness as compared to antharaquinone dyes. This limitation of carbocyclic dyes has been overcome by using heterocyclic coupling or diazonium components in the synthesis of azo dyes. The replacement of a benzene ring by a less aromatic heterocycles in azo dyes results in significant bathochromic shift of the visible absorption spectra and therefore use of heterocyclic coupling and diazo components in synthesis of azo dyes is well-established and resulting dye products are known as heterocyclic azo dyes.

Although, the antharaquinone disperse dyes have excellent properties that are not attainable by azo dyes and have been widely used in cotton or polyester or their blends for military wear automobile seats because of their good fastness properties, the intrinsic disadvantages of antharaquinone dyes of less tinctorial strength because of their small extinction coefficient and complexity of preparation have made their production cost higher than those of azo dyes. Consequently the trends in dyestuff research have been emphasized to improve cost effectiveness and increased technical excellence in terms of high tinctorial strength, brightness, and high fastness properties. This aim is now being realized by replacing tinctorially weak antharaquinone dyes with the tinctorially stronger azo dyes useful for hydrophobic fibers and therefore a sharp increase in the importance of disperse azo dyes 1970s and 1980s attributed directly to the emergence of polyester and nylon as the principal synthetic fibers.
# Table 1.1: Classification of Dyes According to Chemical Constitution

<table>
<thead>
<tr>
<th>Class name of dyes</th>
<th>Characteristic structural unit</th>
<th>Example</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitro</td>
<td>Nitrophenol or Nitroarylamine</td>
<td><img src="image" alt="Naphthol Yellow S" /></td>
<td>Not very fast little commercial importance because of its poor fastness.</td>
</tr>
<tr>
<td>Nitroso</td>
<td>o-Nirosophenol</td>
<td><img src="image" alt="Fast green O" /></td>
<td>Used in dyeing and calico-printing in the form of lakes</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td></td>
<td><img src="image" alt="Cl Solvent Violet 3" /></td>
<td>Deeply colored vats with a wide range of color</td>
</tr>
<tr>
<td>Azo</td>
<td>Monoazo</td>
<td><img src="image" alt="Acid orange H" /></td>
<td>Largest and most varied group of synthetic organic dyes, commercial dyes ranges from yellow to red to blue and green colors for major substrate.</td>
</tr>
<tr>
<td>Class name of dyes</td>
<td>Characteristic structural unit</td>
<td>Example</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>Xanthene</td>
<td><img src="image" alt="Xanthene structure" /></td>
<td><img src="image" alt="Fluorescein" /> Brilliant fluorescent dyes with red to yellow color.</td>
<td></td>
</tr>
<tr>
<td>Thiazoloe</td>
<td><img src="image" alt="Thiazole structure" /></td>
<td><img src="image" alt="Cl Basic Yellow 1" /> Thiazole ring gives increased substantivity.</td>
<td></td>
</tr>
<tr>
<td>Thiazine</td>
<td><img src="image" alt="Thiazine structure" /></td>
<td><img src="image" alt="Cl Basic Blue 9" /> Generally show poor bleach fastness.</td>
<td></td>
</tr>
<tr>
<td>Oxazine</td>
<td><img src="image" alt="Oxazine structure" /></td>
<td><img src="image" alt="Cl Basic Blue 6" /> Generally give poor fastness of the shades to light and alkali.</td>
<td></td>
</tr>
<tr>
<td>Diphenylmethane</td>
<td><img src="image" alt="Diphenylmethane structure" /></td>
<td><img src="image" alt="Cl Basic Yellow 2" /> Only few dyes of this class are commercially important.</td>
<td></td>
</tr>
</tbody>
</table>
### Table 1.2: Classifications of Dyes According to Usage

<table>
<thead>
<tr>
<th>Class</th>
<th>Chemical Types</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Azo, azine, xanthenes, triphenylmethane, nitro and nitroso, antharaquinone,</td>
<td><img src="image" alt="Acid Red 4 (Cl 14710)" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Useful for nylon, wool, silk, paper, ink and leather.</td>
</tr>
<tr>
<td>Reactive</td>
<td>Azo, oxazine, antharaquinone, phthalocyanine,</td>
<td><img src="image" alt="CI Reactive Yellow 17 (Cl 18852)" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Used for dyeing fibers like cotton, wool, silk and nylon</td>
</tr>
<tr>
<td>Basic</td>
<td>Cyanine, hemicyanine, diazahemacyanin, diphenylmethane, triphenylmethane,</td>
<td><img src="image" alt="CI Basic Blue 3 (Cl 51005)" /></td>
</tr>
<tr>
<td></td>
<td>azo, azine, and antharaquinone</td>
<td>Cationic dyes yield intense brilliant shades on cotton, rayon, paper and nylon but fugitive to light.</td>
</tr>
<tr>
<td>Disperse</td>
<td>Azo, styryl, nitro, benzodifuranone antharaquinone,</td>
<td><img src="image" alt="CI Disperse Yellow 241 (Cl 12840)" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Important for dyeing on synthetic fibers such as polyester, polyamide acetate, acrylic and blends.</td>
</tr>
</tbody>
</table>
### Class Chemical Types Example

<table>
<thead>
<tr>
<th>Class</th>
<th>Chemical Types</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>Azo, phthalocyanine, stilbene and oxazine</td>
<td><img src="image" alt="Direct Red 44 (CI 22500)" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Very useful class of dyes for cotton, rayon, paper and nylon.</td>
</tr>
<tr>
<td>Azoic</td>
<td>Azo</td>
<td><img src="image" alt="Naphthol AS" /></td>
</tr>
<tr>
<td>components</td>
<td></td>
<td>Chemically insoluble colored azo pigments used for dyeing and printing cotton, rayon, cellulose acetate and polyester in fast shades</td>
</tr>
<tr>
<td>and</td>
<td></td>
<td></td>
</tr>
<tr>
<td>compositions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td><img src="image" alt="Sulfur" /></td>
<td><img src="image" alt="Vat Antharaquinone and indigosols" /></td>
</tr>
<tr>
<td>Vat</td>
<td>Antharaquinone and indigosols</td>
<td><img src="image" alt="Cl Vat Blue 4 (CI 69800)" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Most valuable for dyeing and printing on cotton, rayon and wool with better fastness.</td>
</tr>
</tbody>
</table>
1.1.2 History and Developments

The first use of insoluble dyes in suspension in aqueous bath to dye cellulose acetate was proposed in 1921 and its commercialization as Duranol dyes was began in 1924 by British Dyestuff Corporation and SRA dyes by British Celanese Company. The appearance of synthetic fibers in the 1920s accelerated the further development of synthetic dyes. Soon after British Celanese succeeded in commercializing cellulose acetate fiber in 1921 disperse dyes for this fiber were invented by Stepherdson (British Dyest Corporation) and Celanese independently. Disperse dyes for polyester fibers were developed after introduction of this fiber by ICI and Dupont in 1952. Development of polyacrylonitrile fiber stimulated the invention of modified disperse dyes in which quaternary ammonium groups are introduced. In 1952, the universally accepted name “Disperse Dyes” was introduced and defined as substantially water insoluble dyes having substantivity for one or more hydrophobic fibers and usually applied from aqueous dispersion. Azo and antharaquinone compounds comprise the two principal structural types which are used as disperse dyes. These dyes are used mainly for the coloring of polyester, nylon, cellulose acetate and triacetate fibers in textile applications. The early yellow disperse dyes were based on phenolic coupling components, CI Disperse yellow 3 still used for dyeing cellulose acetate and nylon fiber. The latter development of commercially important disperse yellow to blue dyes.
Many of the disperse dyes originally developed for cellulose acetate were found to be deficient in light fastness and leveling properties (build up) when applied to polyester fiber. Consequently there has been a steady development of new disperse dyes to meet the demands imposed by changing application methods and to provide much needed importance in fastness properties. Heimann S. have published an excellent review of developments in disperse dyes and their technology. Some successful examples of disperse azo dyes having brightness of color very close to that of antharaquinone reds and blues for polyester. These commercial disperse dyes are of two types mono azo and disazo with the color yellow, orange, red and blue derived from phenolic coupling components. A large number of violet and blue disperse azo dyes are available by using heterocyclic synthesis as dye precursors.

In the 1970s and 1980s disperse dyes were the fastest growing class of dyes due to the fact that they are the only dyes which can be used for dyeing polyester fibers. The development of disperse dyes is the result of the significant increase in the world production of polyester compared to other fibers. The increase of disperse monoazo dyes has been mainly due to the fact that the range of shades obtainable with monoazo dyes has increased bathochromically. Today a large number of violet and blue disperse monoazo dyes are available. Most yellow, orange and red disperse dyes are azo benzene derivatives. N-mono and N- dialkylated anilines are versatile in this respect, as their water solubility can be optimized by the presence of additional substituents in the N-alkyl groups.

The use of nitrodiazobenzene as diazo component is much more frequent with these dyes. One of the first industrial products of this type was Dispersol Fast Scarlet B. Examples for the first type of blue disperse dyes are Resolin Blue BBL5 and Terasil Navy Blue SGL. The strong bathochromic shift between 13, 14 and 15 is due to the additional methoxy and acylamino groups in the 2,5 position of coupling component and the additional electron withdrawing substituents in the diazo component.

Later disperse dyes have gained importance through the use of aromatic heterocyclic compounds as diazo or coupling components. Diazonium salts of 2-aminothiazole, 2-aminobenzthiazoles, 2-aminoisothiazoles, 5-aminopyrazoles, and
2-aminodiazloes have been described in many patents. The use of heteroaromatic diazo components was stimulated by Dickey and Twone that 2-amino-5-nitrothiazole can be used to produce bright violet and blue disperse dyes. The structurally most simple commercial product is Eastman HTP Violet 310 16 48. A very large number of other disperses dyes based on heteroaromatic diazo components and somewhat later also dyes based on heteroaromatic coupling components have been introduced industrially, but only few dyes have been disclosed by the producers. Scientific work on heteroaromatic diazonium ions has been published in reviews. With diazotized aminobenzothiazole and its derivatives orange to violet monoazo dyes can be obtained. A bathochromic shift is observed with nitro substituted isomeric amino benzoisothiazole49. The kinetics and mechanism of the diazotization of 2-aminothiazole were investigated by Dienre et al. and reported the causes for the low yield of diazotization and of consecutive azo coupling reaction of heteroaromatic amine 50. 5-pyrazole, 2-methyl and 2-phenylindole, 1,3,3-trimethylene indolenine, imidazoles, barbituric acid and pyridone derivatives, hydroxy quinolines and quinolines are reported in patents as coupling components 51. Most important yellow disperse dyes based on pyridone derivatives as coupling components are reported for dyeing polyesters. Azo dyes containg heterocyclic rings lead to brighter and often deeper shades than their benzene analogous and they are still very important for applications such as disperse dyes for polyester fiber 52. Therefore they have recently attracted the interest of many research groups.
1.1.3 Color and Structure Relationship

According to general principles of color of azo compounds and their structure, increasing the substitution of the diazo component by electron attracting groups produces diazo component required polarity enables to obtain blue shades from structure such as 17 and 18.  

![Structures 17 and 18](image)

However, utilization of such powerful diazo components poses practically difficulty in coupling reaction. The deep shade is obtained from the coupling components which contain electron releasing groups present in ortho- to the azo linkage. Such groups (-NH$_2$, OH, -CH$_3$, halogen group (-Cl, Br, I) enhance the polarity and therefore produce bathochromic shift. This effect can be further increased by incorporation of amino group into heterocyclic ring to produce heterocyclic diazo components. Such diazonium components are capable of producing remarkable bathochromic shifts compared with the corresponding benzenoid compounds. For examples dyes prepared by coupling diazotized 5-substituted-2-amino -3-nitrothiophenes 19 or 2-amino-5-nitrothiazole 20 with simple arylamine coupling component 21 are blue to greenish blue in color.

![Structures 19, 20, and 21](image)

In these dyes the heteroatoms in place of negative substituents enables deep shades to be successfully obtained from highly polar dyes of low molecular weight and fulfill the need of dyeing efficiency. Consequently dyes with heterocyclic diazo components have received much attention since they offer high tinctorial power, excellent brightness and fastness and commercially competitive with more expensive with more anthraquinine dyes. Therefore innovation in the field of disperse dyes...
derived from heterocyclic diazocomponents has significantly the replaced antharaquinone red and blue colorants of textile. However research continues unabated in response to the increased demands of disperse dyes greater use of blends and finishing treatment, better dye performance and fastness. Besides this textile industries are still looking for brighter, more cost effective colorants which can add value to substrates as well as meet the ever increasing demands of consumers dyers and legis laters. Therefore there is a motivating drive to hetaryl azo dye research for both industry and academic. In this context, literature survey has featured considerable growth in academic research of synthesis, properties and application of hetarylazo dyes in the last two decades.

1.1.4 Dyeing Fibers With Disperse Dyes

The advent of synthetic fibers led the development of special classes of dyestuffs designed for their coloration, while the dye classes which can be applied vary from fiber to fiber according to its nature. The tendency of a textile fiber to absorb a dye from aqueous solution and to retain it is the basis of normal dyeing processes. The nature of absorption (or substantivity) of dyes of various types by the natural and synthetic fiber is dependent on the chemical constitution and fine structure of the fiber, as well as on the chemical constitution of dye and its structure in aqueous solution, it is also influenced by the added substances and conditions of the dyeing treatment. Thus substantivity is not an absolute property.

Ionization of dyes in aqueous solution is a characteristic of the dyes having affinity for cotton; wool and silk for example direct dyes, acid dyes and basic dyes. Textile fibers like cotton and wool composed of linear polymer of high molecular weight when placed in water, it is wetted, water is absorbed and the osmotic pressure swells the fiber. Dealing with aqueous solution of dye, the degree of wetting and absorption will depend on the nature of the dye and the fibre as well as temperature.

Disperse dyes emerge as a fairly common class of dyes for application to the majority of synthetic fibers (cellulose, di- and triacetates, polyester, polyamide) and to some extent on acrylic fibers. They are indeed practically the only useful class of dyestuff. Disperse dyes initially were of fairly small molecular size in order to achieve satisfactory dye uptake by fiber to yield deep shades like navy blue and black.
However it was difficult to prepare dyes of this type. For this reason it was necessary to search novel coupling and diazonium components instead of using classic type organic components. In addition to this, fibers exist as natural, or synthetic, hydrophilic, hydrophobic, nonionic and ionic. Natural fibers have complex chemical structure and difficult to characterize it. Consequently dyeing of natural fibers is much more complex than dyeing of synthetic fibers. Hydrophilic fibers are hydrated and need water soluble dyestuff. The water solubility is brought about by introducing ionic groups either cationic or anionic into molecule. Hydrophobic fibers are difficult to dye with ionic or hydrophilic dyes. Therefore nonionic hydrophobic dyes are used for these fibers. However a modified polyester or polyamide fiber (nylon) makes these fibers capable of being dyed by water soluble dyes. Therefore in 1970s and 1980s the sharp increase in the importance of disperse dyes can be attributed directly to the emergence of polyester and nylon as the principal synthetic fibers.

Disperse dyes commonly used to dye polyester are nonionic and dye the polyester fiber through a diffusion mechanism. Prolonged boiling of the dye bath solution loosens the forces binding the polymeric chains to each other, causing fiber to swell resulting into limited penetration of dye into fiber. Further the rate of diffusion of disperse dyes in polyester is much lower than that on nylon and cellulose triacetate fibers. In other words low rate dyeing increases the cost as well as gives dull shades with poor fastness properties. Deep shades and good fastness properties on polyester can be achieved by using disperse dyes in presences of carriers, or high temperature dyeing techniques with or without carriers. Dye carriers promote dye migration and transfer to produce level and satisfactory dyeing. Using greatly improved methods of dispersion many of dyes for acetate have been used for polyester fiber. However the use of carriers, high temperatures and pressures the stringent requirements in the dyeing processes have led to the synthesis of many new dyes specifically designed for polyester fibers. Of these disperse dyes are mainly azo dyes and anthraquinine derivatives. Azo dyes from low molecular weight heterocyclic intermediates either as diazonium components and coupling components for a mono azo dyes produces a profound bathochromic shift from red to blue.

Since 1950, there has been a steady development of new disperse dyes to meet the demands imposed by the changing application methods and to provide the much...
needed improvement in fastness properties. Six different methods of applying disperse dyes have been developed are \(^5^7\): (1) Dyeing at the boil in the presence of a carrier is used for delicate fabrics such as polyester-wool blends. (2) Dyeing at 120-135 °C in pressurized vessels gives better exhaustion and often improved fastness to light, rubbing, and perspiration. (3) Thermo fixation techniques at 190-200 °C are used for the continuous processing of certain types of fabrics. (4) Transfer printing, generally at 210°C for 30 seconds, is an important development. (5) Solvent dyeing methods are available, but are not popular. (6) Printing and continuous dyeing processes have been developed for polyester-cotton blends using specialist dyes and application techniques such as Dybln (DuPont), Calestren (BASF), and Dispersol (ICI) ranges. The polyamide is the most hydrophilic of the synthetic fibers and it can be dyed with disperse, direct, acid and metalized dyes. Of these two most useful classes are the disperse dyes and acid dyes. The disperse dyes have the better dyeing properties but are somewhat deficient in fastness properties, the acid dyes have much better fastness properties but are generally inferior in dyeing behaviour due to irregularities in nylon fiber. The insoluble hydrophobic disperse dyes readily dye nylon because their mode of attraction is completely nonionic and are completely insensitive to chemical variations and pH. Small molecular sized disperse dyes show high rates of diffusion and excellent migration properties at high temperature of dyeing but it can readily described to give poor fastness properties due to open structure of nylon and dyes can freely more within the non-crystalline region \(^5^8\).

1.1.5 Market Survey

Global demand for dyes and organic pigments is forecast to grow 3.9 percent annually through 2013. Dyestuff can be used for printing inks, plastics, textiles, paper and foodstuff. The world consumption for dyestuff accounts for printing inks at 40%, paints 30%, plastics 20% and others from segments like textiles. China, Taiwan, India, Japan, Korea and Pakistan are the major dyestuff producing countries in the industry. The Asia/Pacific region will lead gains and increase its market share to one-half of world demand by 2013. China is by far the largest single consumer in the world and fast growing national market. Strong gains will also occur in other developing areas such as Africa/Mideast region and Eastern Europe, while market maturity will limit advances in developed areas such as North America, Western Europe and Japan.
The dyestuff industry constitutes an important segment of the chemical industry in India. The Indian dyestuff industry is today totally self-sufficient with a majority of its inputs manufactured locally. India is currently producing all varieties of synthetic dyestuffs and intermediates and has a small presence in the natural dyestuff. The subcontinent has emerged as a global supplier of dyestuffs and dye intermediates, particularly for reactive, acid, vat and direct dyes. The dyestuff industry in India is mostly located in Gujarat and Maharashtra. Gujarat comprises of more than 1200 small scale industrial and factory sector units. There are about 158 large scale projects involving an investment of INR 14.06 billion which have been commissioned. The dyestuff industry in Gujarat substantially contributes in production as well as to the domestic consumption and export basket of the country’s target.

Over the last 15 years the Indian dyestuff industry has established itself in the export arena and among the various types of dyes exported, export of reactive dyes accounts for the largest share and growth. In the recent past Indian dyestuff industry has been facing competition from China, Korea, Thailand, Taiwan and Pakistan. Industry experts believe that dyestuff industry in India can be a real force to reckon with in exports and in 2009-10 its exports may increase up to 10% of the world’s market share. The major domestic markets are Rajasthan, Gujarat, Maharashtra, Tamil Nadu, Haryana and Uttar Pradesh where as the overseas market are Europe, USA, Indonesia, Honkong, South Korea, Egypt and Africa. India has become a major player in the export of disperse, reactive, acid and vat dyes. Therefore focus on the production of acid, basic, direct and reactive dyes as these are economical whereas big companies concentrate on vat, solvent and disperse dyes.

In textile, cotton and polyester consume more dye compared to the other fabrics and in turn the growth of disperse, direct and reactive dyes will increase due to the usage of these intermediates in cotton and polyester. In future, the contributions for disperse dyes will be more followed by direct dyes and reactive dyes. Table 1.3. furnishes the various units in the organized sector engaged in the manufacture of disperse dyes.
Table 1.3: Dye Stuff Industries in India

9. M/s Sandoz (India) Ltd., Sandoz House, Dr. A.B. Road, Worli, Mumbai-400018.
1.2 Recent Developments

Heterocyclic Disperse Azo Dyes (1990 on Words)

Most hetaryl azo dyes of technical interest for application to textiles are derived from diazo components consisting of five membered rings with sulphur or nitrogen heteroatom to which a diazotizable amino group is directly attached and ring be fused to another aromatic ring. For examples benzothiazoles, benzoisothiazole, thiazoles, thiophenes etc. Dyes prepared from 2-aminothiazoles and 2-aminobenzthiazoles have a long history and a significant role in disperse dyes technology. Developments in the field of hetarylazo disperse dyes first started with the use of 2-aminobenzthiazole derivatives to give commercially technically important dyes CI Disperse red 177 and CI Disperse Blue 339 for polyester. Many disperse mono azo dyes used for dyeing polyester are synthesized from various heterocyclic compounds as diazonium components and coupling components (Table 1.4).

A single azo group is inadequate for the production of substantivity necessary for practical dyeing, unless other groups favourable to substantivity are also present. Azo dyes show good substantivity if they contain two or more azo groups or monoazo dyes with specific constitutional factors such as thiazole rings or amide group. Azo dyes based on heterocyclic amines have been developed and the resultant dyes give higher tinctorial strength and brighter dyeing than those derived from aniline based diazocomponents. For instance amino substituted thiazole, isothiazole, thiophene compounds afford highly electronegative diazo compounds and consequently provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds. Although, many patents and papers describe the synthesis and dyeing properties of monoazo heterocyclic dyes, very few comparable investigations have been made with disazo heterocyclic dyes. Only a few disazo disperse dyes have been used as commercial products. We have previously reported the synthesis of various heteroaryl azo disperses and acid dyes derived from Mannich base intermediates. Continuing our earlier studies designed to prepare new disazo disperse dyes for dyeing polyester and nylon fabrics, we have carried out the synthesis.
Table 1.4: Disperse monoazo dyes

<table>
<thead>
<tr>
<th>CI Disperse Red 177</th>
<th>CI Disperse Blue 339</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Image of CI Disperse Red 177" /></td>
<td><img src="image2" alt="Image of CI Disperse Blue 339" /></td>
</tr>
</tbody>
</table>

**2- amino thiadiazoles**

<table>
<thead>
<tr>
<th><img src="image3" alt="Image of 2-amino thiadiazole" /></th>
<th><img src="image4" alt="Image of 2-aminothiazolo[5,4-c]pyridine" /></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = H, CH_3$; $R_1 = H_2$; $R_2 = H, OH$</td>
<td>$R_1 = R_2 = H, CH_3, C_2H_5, C_3H_6OH, CN$</td>
</tr>
</tbody>
</table>

**2- amino thiazole**

<table>
<thead>
<tr>
<th><img src="image5" alt="Image of 2-amino thiazole" /></th>
<th><img src="image6" alt="Image of 2-aminothiazolo[5,4-c]pyridine" /></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1 = H, NHCOCH_3, NHCOC_2H_5, NHCOH_5$; $R_2 = H, NO_2, Et$</td>
<td>$R_1 = H, NHCOCH_3, NHCOC_2H_5, NHCOH_5$; $R_2 = H, NO_2, Et$</td>
</tr>
</tbody>
</table>

**2-aminothiazolo[5,4-c]pyridine**

<table>
<thead>
<tr>
<th><img src="image7" alt="Image of 2-aminothiazolo[5,4-c]pyridine" /></th>
<th><img src="image8" alt="Image of 4,5,6,7-tetrahydrobenzthiazole" /></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1 = R_2 = H, CH_3, C_2H_5, C_3H_6OH, CN$</td>
<td>$R_1 = R_3 = H, OCOCH_3, CN$; $R_2 = H, OCH_3$; $R_4 = H, Cl$</td>
</tr>
</tbody>
</table>

**2- amino thiazole**

<table>
<thead>
<tr>
<th><img src="image9" alt="Image of 2-amino thiazole" /></th>
<th><img src="image10" alt="Image of Azobenzthiazole" /></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = OM_S, Br$; $R_2 = H, Br$</td>
<td>$R_1 = H, NO_2$; $R_2 = H, 2-CH_3OH, (2-CH_3, 3-Cl, 4-Cl)$; $R_1 = Cl, CF_3, CN, NO_2$; $R_2 = 4-I, 3-CH_3OH, 4-NO_2, (2-CH_3, 4-I)$; $R_3 = NHCOCH_3, (2-CH_3, 4-I)$; $R_4 = (2-CH_3, 4-I)$CH_3</td>
</tr>
</tbody>
</table>

**Azobenzthiazole**

Department of Chemistry, S. P. U.

22
Chapter 1

Department of Chemistry, S. P. U.

2-aminothiazole

$R_1 = H, Me \quad R_2 = Me, H \quad R_3 = Me, EtCOCH_3, Ph \quad R_4 = 4-ClC_6H_4, 4-BrC_6H_4$

$a$-amino-cyano-pyrazoles

$R = CO_2H, NO_2 \quad R_1 = H, NHCOPh \quad R_2 = CN, CONH_2$

5-amino-pyrazole

$R = H, (\alpha-, \beta-, \gamma-OCH_3), (\alpha-, \beta-, \gamma-Cl), (\alpha-, \beta-, \gamma-CH_3), (\alpha-, \beta-, \gamma-NO_2)$

Substituted benzimidazole

1-substituted hydroxy pyridone

$R = H, CH_3, CH_2CH_3, CH_2CH_2CH_2OCH_3$

5-amino-2-pyridone

$R_1 = H, CH_3 \quad R_2 = CH_3H \quad X = O, CH_2$

Bithiophene azo dyes

$R_1 = NMe_2, NEt_2, Pyrrolidine, Piperidine \quad R_2 = 3-CO_2H, 4-CO_2Me, 4-CN, 4-NO_2$

Phthaliamide azo dyes

$R = CH_3CH_2CH_2CH_2, CH_3(CH_2CH_2)CH_3, CH_3CH=CH_2 \quad R_1 = R_3 = H, Br, CN \quad R_2 = H, -NHAc$
and characterization of a family of new disazo dyes based on Mannich bases and study of their dyeing properties on polyester and nylon fibers. Therefore in the present section a brief literature review regarding disazo disperse dyes is given.

A. T. Peters and E. Chisowa \(^{20}\) have reported the synthesis of a series of disazo dyes of general formula 22 derived from monoazo structure 23 and evaluated the effect of substituents on the color of dyes. They reported that the disazo analogues have not been extensively described but typically the use of 5, 6-disubstituted-2-aminothiazoles affords useful dichroic dyes absorbing above 600 nm.

Jolanta and coworkers \(^{81}\) reported the synthesis and evaluation of some red, violet and bluish violet disperse disazo dyes 24 based on derivatives of 2-amino-6-phenyl azo benzothiazole and its nitro substituted analogues. The spectral properties and the basic fastness properties of the dyes on polyester fiber are also discussed in terms of their chemical structure.

Pi Chen Tsai and coworker \(^{82}\) have reported the synthesis of a number 3, 6 disubstituted-azoyl-2,5,7-triamino pyrazolo [1,5-a] pyrimidine heterocyclic disazo dyes 25 and 26 with different arylazo and hetarylazo groups in 3,6-position respectively and studied their solvatochromic behavior in various solvents.
Heterocycles containing pyrimidine moieties stand as an ever-expanding area of research in a large number of pharmaceutical agents, natural products and as intermediates in the dyestuff industries. Some azopyrazole derivatives also find application in dyes and complexes. F. Karci and coworkers have used amino pyrazole compounds as intermediates in synthesis of various new disazo pyrazolol [1, 5-a] pyrimidine derivatives are 27-31.

The 4-aryl pyrazolones were used as dyes for all kinds of fibers, whether natural or synthetic. A number of 4-arylazo-pyrazolin-5-ones have been reported in the literature due to the application of most of them as dyes of commercial value. In this context, M. A. Metwally and coworkers have reported the synthesis of new 4,4′-bisazo (o-, m-, and p-phenylene) derivatives 32 and 33 of 4-hydroxymethyl-2-pyrazolin-5-one and investigated for their dyeing performance on polyester fabrics. The dyed fabrics exhibit very good to excellent washing, perspiration and sublimation fastness properties. The ease of preparation of such dyes makes them particularly valuable.
The use of heterocyclic Mannich bases intermediates in the synthesis of azo dyes is reported in the patent. Tadashi Saito and coworkers made patents for the diazoprinting material which was prepared by using a number of coupling components containing Mannich base structure of following general formula 34. The photoprinting material thus obtained gave dyes, dark blue dye image of good quality. Iroh Yamase and coworkers synthesized several reactive dyes containing \(-\text{NH}_2\) or \(-\text{OH}\) group. These dyes were obtained by the Mannich condensation of azo dyes containing acetophenone groups with dimethylamino hydrochloride (Me₂NH-HCl) and paraformaldehyde using molar ratio 1:1:1:2.5 in acetic acid or water- dioxane solvent with concentrated HCl (Scheme 1.1). The reactive dyeing with these dyes was carried out on nylon 6, silk and viscose rayon and their applicabilities color and fastness were examined. These dyes were fixed well and showed excellent fastness especially in case of nylon-6.

\[ R = \text{Alkyl group 1 to 4 carbon atoms} \quad R_1 = \text{H, lower alkyl, aryalkyl} \]
\[ R_2, R_3 = \text{5 or 6 membered heterocyclic ring, Morpholine, pyrididine} \]

**Scheme 1.1: Mannich Base**
Present work
A brief summary of work presented in the thesis is given have in the following:

Part I of thesis deals with synthesis and characterization of eight series of azo disperse dyes derived from Mannich base intermediates as diazoni um compounds.

Chapter 1 describes an overview of azo disperse dyes with respect to their general background, chemistry and its importance in textiles dyeing and high-tech materials as well as recent developments and economic aspect and environmental concerns.

Chapter 2 comprises the systematic work carried out for the synthesis and characterization of new disperse disazo dyes. It includes the synthesis of eight parent dihydropyrimidinones/thiones (DHMPs) by Biginelli reaction of aromatic aldehydes namely benzaldehyde, salicyaldehyde, p-anisaldehyde, and vanillin with ethylacetoacetate and urea/thiourea respectively in the presence of HCl as a catalyst. These DHMPs have been subsequently used as an active hydrogen substrate in Mannich reaction with p-phenylenediamine and formaldehyde in presence of hydrochloric acid as catalyst to yield Mannich bases \(1a-d\) and \(2a-d\). These Mannich base \(1a-d\) and \(2a-d\) have been used as a diazonium component in coupling reaction with ten aromatic hydroxy derivatives resulted into a formation of a family of two groups of disazo disperse dyes (MBUD- and MBTD- groups) consisting of four series of disperse disazo dyes in each group. They are assigned as \(1a-, 1b-, 1c-, and 1d-series\) (MBUD-group) and \(2a-, 2b-, 2c-, and 2d-series\) (MBTD-group).

Parent DHMPs, Mannich bases and disazo disperse dyes are characterized for their general properties (melting point, solubility, number of azo groups and TLC) and chemical structure by elemental analysis and spectral studies (UV-visible, IR, \(^1\)H NMR, \(^{13}\)C NMR and Mass).

Chapter 3 deals with the study of dyeing properties of disazo disperse dyes on polyester and nylon fabrics using high temperature dyeing method. The applicabilities of these new disazo disperse dyes have been evaluated by exhaustion and fixation studies of dye as well as by estimation of the fastness properties (wash fastness, light fastness and rubbing fastness) of dyed fabrics using standard methods.
Part II of the thesis comprises the removal of synthetic dyes such as reactive dyes, acid dyes, direct dyes and cationic and anionic dyes from aqueous solution using novel chemically modified cationic exchangers of poly styrene-DVB as an adsorbent. In this connection,

Chapter 4 describes a review in brief regarding recent research and developments in the field of water effluent treatment technologies for removal of dyes and their significance to control environmental pollution.

Chapter 5 describes the application of chemically modified ps-DVB cation exchangers (CES) synthesized in our laboratory. These CES have already been investigated for their application as catalysts and as ion exchanger for removal of metals. This work has been further extended in the direction to investigate their application in removal of synthetic dyes from aqueous solutions. Consequently, the work includes two parts; the first part is related to the synthesis and characterization of chemically modified ps-DVB cation exchangers. Chemical modification of commercial choloromethylated ps-DVB by condensation reaction with different amino aromatic sulphonic acids to yield sulphonic acid anchored ps-DVB cation exchangers. Six derivatives of amino aromatic sulphonic acid used are sulphanilic acid, Tobias acid, Peri acid, Gamma acid, H-acid and Chicago acid to yield corresponding cation exchangers (A₁-A₆). These CES have been characterized for their chemical structure (elemental analysis and IR), thermal stability by TGA and surface morphology by SEM. The second part of the work in this chapter presents the investigations regarding the application of new CES for the decolorization of aqueous solutions of synthetic dyes. For this purpose, batch adsorption experiments have been carried out for the removal of two classes of dyes (cationic and anionic) from aqueous solutions using cation exchangers (A₁-A₆) as adsorbent. Studies concerning the effects of pH, cation exchanger dose, initial dye concentration and contact time are also presented and discussed. As effective applications of sorbent require more detailed knowledge of sorption mechanism, the equilibrium isotherms and kinetic study were performed. The adsorption isotherms are described by the Langmuir and Freundlich isotherm models. The pseudo first-order and pseudo second-order models were tested to fit the experimental kinetic dependencies. An intraparticle diffusion model was also used to examine diffusion processes affecting the rate of dye sorption.
References


Chapter 1


