The title of the Section I suggests that the present work is connected with the Heterocyclic azo dyes. Hence it is proper to review briefly about the dyes and more particular heterocyclic dyes.

1 Heterocyclic azo dyes

Color has played a vital role in human history. From the earliest of times, people admired the beautiful natural colors of the plants and minerals. Different types of natural coloring matters to dye clothes prepared from different natural textile fabrics\(^1\). With the growth of intelligence in man, he must have also noticed that most of the colors he saw in nature were not permanent. There might have been an urge in him to try to retain the pleasing colors for longer periods.

The first synthetic dye, Mauvine was discovered by Perkin and led to the many investigations of derivatives of coal-tar as potential coloring matters. In 1771 Woulfe prepared picric acid by the action of nitric acid on indigo and dyed silk in bright yellow shades.

In early days dyes industry saw the discovery of the principal dye chromogens\(^2\). The introduction of synthetic fibers, nylon, polyester and polyacrylonitrile produced the next significant challenge particular to synthetic dyes. Out of these two most important fibers are cotton and polyester. Consequently the manufacturers focused on producing dyes for these fibers and accelerated further research.

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 brightness, high tintorial strength and high fastness properties. This aim has been realized by replacing tintorially weak antharaquinone dyes with the tintorially stronger azo dyes\(^3\).

Today heteroaryl disperse azo dyes are all-pervasive, either as chromophores 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. In addition, these dyes have also been used in functional dyes applications, reprographic technology and photodynamic therapy. Many general reviews on synthesis, properties and applications of heterocyclic disperse azo dyes are appeared in the literature. Many heteroaryl azo dyes of technical interest for application to textiles are synthesized from heteroarylaminino 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.

1.1 Classification of dyes - An Overview

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 such as azo, nitro, nitroso, carbonyl etc. In addition, the dye molecule can also contain auxochrome groups such as amino, alkyl amino, hydroxyl, sulfonic and carboxyl to enhance the chromophore effect. The discussion of different aspects of dyes and pigments regarding chemistry, chemical structure, classification, dyeing properties, applications and their manufacturing and dyeing processes.

Classification of dyes based upon application 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 promote their products under name based on
usage such as acid, basic, direct, disperse, reactive dyes etc.\textsuperscript{9}.

Anthraquinone is the basic unit of commercial trade name dyes. Dyes containing anthraquinone unit belong to mordant, disperse and vat dyes. Anthraquinone dyes have excellent fastness properties. Although, the intrinsic disadvantages of antharaquinone dyes is less tintorial strength and production cost is higher. Consequently the trends in dyestuff research have been emphasized to improve cost effectiveness and increased technical excellence in terms of high tintorial strength, brightness and high fastness properties. This aim is now being realized by replacing tintorially weak antharaquinone dyes with the tintorially stronger azo dyes useful for hydrophobic fibers and therefore a sharp increase in the importance of disperse azo dyes.

1.1.1 Azo dyes

Azo dyes are classified as to indicate the chief method of application into use as acid, base (cationic), direct, disperse, mordent and reactive dyeing classes. From the chemistry viewpoint the disperse azo dyes are divided according to number of azo groups as monoazo, bisazo, trisazo, tetrakis or polyazo dyes and as further subdivided into carbocyclic and heterocyclic (heteroaryl) azo dyes according to the aromatic or heterocyclic radical present in a dye molecule. Because of its cost effectiveness, tintorial strength, brightness, and high fastness properties, they are used to color the vast majorities of apparel and household textiles as well as nontextile materials such as paper, leather, foods, drugs, cosmetics and color photography and constitute the largest group of synthetic dyes both in number and in commercial volume\textsuperscript{10,11}.

1.1.1.1. Monoazo dyes

It is the largest group of dyes, with -N=N- as a chromophore, in an aromatic system. These dyes contain one azo -N=N- group. These dyes cover a full range of bright shade, with good fastness properties.
About 50% of the disperse dyes commercially available are of monoazo type\(^{12}\). They are represented by the general formula (1).

![Formula 1](image)

\( R = \text{Various derivatives of } N\text{-maleimides} \)

Commercial products are generally represented by structure (1). The shade of the dyes of formula (2) depend largely on the substituent \( X, Y, A, B, R^1 \) and \( R^2 \).

![Formula 2](image)

The effect of various substituents in the amino azobenzene moiety in obtaining variety of shades on hydrophobic fibers is well documented in the literature\(^ {13}\). A few examples are listed (3–5).

![Formula 3](image)

![Formula 4](image)

![Formula 5](image)

In comparison to aminobenzenes, aminonaphthalenes have played a minor role as coupling component for disperse dyes and are encountered in only a few industrial applications e.g. (6,7)\(^ {14}\).
Brilliant orange and red shades are obtained when 2-hydroxy naphthalene and its derivatives are used as coupling components e.g. (8-9)\textsuperscript{15}. These dyes have good sublimation fastness.

\begin{center}
\begin{tabular}{cc}
\includegraphics[width=0.4\textwidth]{image1} & \includegraphics[width=0.4\textwidth]{image2}
\end{tabular}
\end{center}

(A) Heterocyclic components

Disperse dyes have gained importance through the use of aromatic heterocyclic compounds as diazo or coupling components such as 2-aminothiazole, 2-aminobenzthiazoles, 2-aminoisothiazoles, 5-aminopyrazoles and 2-aminodiazoles. The use of heteroaromatic diazo component 2-amino-5-nitrothiazole can be used to produce bright violet and blue disperse dyes. With diazotized aminobenzthiazole and its derivatives orange to violet monoazo dyes can be obtained. A bathochromic shift is observed with nitro substituted isomeric aminobenzoisothiazole\textsuperscript{16}. 5-pyrazole, 2-methyl and 2-phenylindole, 1,3,3-trimethylene indolenine, imidazoles, barbituric acid, pyridone derivatives, hydroxy quinolines and quinolines are reported as coupling components\textsuperscript{17}. Azo dyes contain heterocyclic rings lead to brighter and deeper shades and also very important as disperse dyes for polyester fiber\textsuperscript{18}.
Interest in heterocyclic amines as a diazo component has increased recently because of the deep shades, high tintorial power and excellent fastness of the derived dyes. The synthesis and application of heterocyclic diazo components for the preparation of disperse dyes has been reviewed\(^\text{19}\). Blue dyeing on polyester is obtained by using heterocycles as diazo component e.g. (10)\(^\text{20}\).

In addition to 6-nitro, 6-methyl sulfonyl and 6-thiocyanate groups and those with one or two halogens in various position on the benzene ring of benzothiazole nucleus, substituents such as 6-methoxy\(^\text{21}\), 4-nitro-6-methoxy\(^\text{19}\), 4-trifluoromethyl\(^\text{22}\), 5-nitro\(^\text{23}\), 4-N-morpholino-, 6-N-morpholino-, 4-N-piperidino- and 6-N-piperidino-\(^\text{20}\), 4-nitro\(^\text{24}\) and 6-bromo\(^\text{25}\) have been used to prepare the brilliant azo dyes.

The dyes having general formula (11) and (12) have been obtained by using 2-aminobenzothiazole-3-N-oxide, 2-aminonaphthothiazole-3-N-oxide and their 5-nitro derivatives\(^\text{26}\).

Disperse dyes derived from amino isothiazole have received considerable attention on account of their bright shades with good fastness properties e.g. (13)\(^\text{27}\).
The monoazo disperse dyes derived from 2-amino-5-nitrothiazole have been reported. Azo dyes derived from 1-(2'-benzothiazolyl)-3-methyl-5-pyrazolone have been recently reported. 2-Aminothiazoles give brilliant scarlet red to bluish red dyeing on polyester depending on the substituents present in the fifth position of the thiazole moiety and the coupler used e.g. (14)\textsuperscript{30}.

\[ \text{NR}_2 = \text{NMe}_2, \text{NPh}_2, \text{Morpholine} \]

The dyes derived from di- or tri-substituted -2-aminothiophenes as diazo components have been reported. Typical examples are (15)\textsuperscript{31} and (16)\textsuperscript{32}.

Where \( R_1 = 5\text{-nitrothiazole, 5-nitrobenzothiazole} \)

Recently a series of thienylazo dyes has been prepared from nitro-substituted 2- and 3-aminothiophenes; colorants from the former were reddish blue to green, whereas those from the latter were yellow to orange. A series of monoazo dyes has been synthesized from
2- and 3-aminobenzothiophene diazo components\textsuperscript{34}. In the last few years, some novel heterocyclic amines have been used as diazo components in the synthesis of azo disperse dyes\textsuperscript{35}.

The heterocyclic diazo components based on 2-amino-4,5-dicyano imidazoles, 2-(o-amino-phenyl) benzimidazole, 3-amino pyrazoles, 5-amino pyrazoles, 6-amino-2-methyl-4-oxoquinazoline and 2-methyl-3-(4''-amino -4'-benzanilid-1'-yl)-4-oxoquinazoline, have also been used\textsuperscript{36}.

**(Bb) Heterocyclic coupling components**

Heterocyclic coupling components give heterocyclic azo disperse dyes with color ranging from yellow to deep red. Orange dyes have been obtained by using aminopyrazoles\textsuperscript{37} as coupling components which are suitable for polyester fabric, e.g. (17).

![17](image)

The hydroxy pyridones\textsuperscript{38} as heterocyclic components enable intense greenish yellow azo dyes, e.g (18).

![18](image)

The azo pyridone dyes\textsuperscript{39} derived by the coupling of 3-cyano-6-hydroxy-4-methyl-2(1\textit{H})-pyridone with diazotized para and meta substituted anilines have been reported. Recently the preparation and use of pyridone azo dyes\textsuperscript{40} have also been reported e.g. (19).
Coupling components based on 2-N, N-dialkylaminothiazoles have attained technical importance as terminal coupling components for blue azo dyes for polyester-cellulose blended fabrics\(^41\). Monoazo dyes with heterocyclic\(^42\) diazo components have also been patented. Heterocyclic groups have been introduced into the 4\(^{th}\) position of the thiazole coupling components\(^43\). 2-N, N-dialkylaminothiophenes with various substituent in the 3\(^{rd}\) position and alkyl or phenyl groups in the 4\(^{th}\) position were coupled with heterocyclic diazo components\(^44\). Yellow dyes with greener hues are brighter than obtained from pyrazolones can be obtained from 4-hydroxyquinolone e.g. (20)\(^45\).

Several heterocyclic coupling components (21) have been used based upon the benzimidazole substituted pyridine\(^46\), 4-hydroxy-1-methyl-2-oxiquinoline\(^47\), 2-cyanomethyl-4-oxiquinazoline\(^48\), 2-hydroxypyridine, 2-aminopyridine\(^49\) and N-phenylaziridine\(^50\).
1.1.1.2 Bisazo dyes

Several research activities are going on worldwide to synthesize bisazo disperse dyes with improved fastness properties and bright hues. Most of the bisazo disperse dyes have been derived from simple and cheap intermediates. These dyes when derived from aromatic components provide mainly yellow, orange and red hues and when derived from heterocyclic components provide red, violet and blue hues with good fastness properties. Structures of simple bisazo disperse dyes (22) were derived from aromatic components with phenol as end coupler\textsuperscript{51}.

![Structure of bisazo dye (22)](image)

where, \( R = \) phenol, 4-nitrophenol, 2-naphthol, 2-cresol, 4-cresol, resorsinol, 2-chlorophenol, 3-aminophenol

The dye structures have been modified to achieve desirable fastness properties by either increasing the molecular weight or by introducing more polar groups and by decreasing their undesirable weak solubility in water. The introduction of the polar group into dye molecule yields good fastness to light and sublimation.

Patel et al., have synthesized bisazo dyes (23) by coupling tetrazotised 4,4'-diaminodiphenyl sulphonamide with o-fluoroanilino cyanurated coupling component, and their dyeing performance on silk, wool and cotton fibers has been assessed\textsuperscript{52}.

![Structure of bisazo dye (23)](image)

where, \( R = o\)-fluoroaniline
The replacements of central phenyl ring of a bisazo disperse dyes by heterocycles causes marked bathochromic shift\textsuperscript{53}. Disperse dyes (24-25) are the examples which show a distinct change in hue by replacement of phenyl ring by thiophene or thiazole.

Patel et al., have been synthesized bisazo dyes (26) by coupling tetrazotized 4, 4’-methylene bis 2, 5-dichloroaniline with various m-toluidino cyanurated coupling component for silk, wool and cotton fabrics\textsuperscript{54}.

Kim T. and co-worker\textsuperscript{55} have synthesized bisazo dyes of following structure (27). The fastness properties are also reported.
Patel D.R. and co-worker\textsuperscript{56} have synthesized hot brand bisazo dyes (28). These dyes were applied on fibers. The fastness properties, exhaustion and fixation data were also been studied.

\begin{center}
\includegraphics[width=\textwidth]{28.png}
\end{center}

Shams H.Z.\textsuperscript{57}, has synthesized bisazo dyes (29) using pyrazolo [1, 2-a] pyrazole fused system as chromophoric moiety. The synthesized dyes were applied to cotton fabrics under the typical exhaust dyeing condition and fastness properties were investigated.

\begin{center}
\includegraphics[width=\textwidth]{29.png}
\end{center}

Mokhtari J. and co-worker\textsuperscript{58} have synthesized trisazo hetero bifunctional dyes (30) based on J-acid. The dyeing properties have also been reported.

\begin{center}
\includegraphics[width=\textwidth]{30.png}
\end{center}

where, $X = H, SO_3H$
\begin{itemize}
  \item $Y = H, CH_3$
  \item $Z = SO_2CH_2CH_2OSO_3H$
\end{itemize}
Various heterocyclic components are incorporated in the recent development of bisazo disperse dyes. The heterocyclic moiety may involve as the first component, middle component as well as end component of bisazo disperse dyes with remarkable properties such as brightness of their shades and excellent fastness. Among the various heterocycles incorporated in the bisazo disperse dyes; thiophene, pyridine, thiazole, quinolinone, pyrazole, benzothiophene, imidazole, benzothiazole and fused heterocyclic systems find great importance.

Rangnekar and Puro\textsuperscript{59} have synthesized fused heterocyclic bisazo disperse dye (31) which gives yellow to orange shades on polyester with good fastness properties.

![Chemical Structure 31]

Fused thiazole heterocycle\textsuperscript{60} have been used as middle component to prepare blue bisazo disperse dyes with excellent fastness properties e.g. navy blue bisazo dye (32).

![Chemical Structure 32]

Various isothiazole derivatives have been reported to give red to blue bisazo disperse dyes\textsuperscript{61}. Pyrazole derivatives are also utilized to prepare orange to red bisazo disperse dyes, both as bisazo\textsuperscript{62} and coupling component\textsuperscript{63}. Imidazole derivatives have also been used to prepare bisazo disperse dye\textsuperscript{64}. 
Bisazo disperse dye (33)\textsuperscript{65} using quinazolinone is reported to show excellent fastness properties.

![Chemical Structure of 33](image)

Now a days trade come for various heterocyclic dyes which also include pyridone azo dyes. There are many mono and bisazo pyridone dyes available. Now here we focus on pyridone azo dyes.

1.1.1.3 Pyridone azo dyes

Pyridone derivatives are relatively recent heterocyclic intermediates for the preparation of dyes. Pyridone found wide utilization in textile industry for azo and azomethine dyes\textsuperscript{66}. The arylazo pyridone dyes present are very important class of colorants. The success of azo colorants is due to the simplicity of their synthesis by diazotization and azo coupling, to the almost innumerable possibilities presented by variation on the diazo compounds and coupling components, to the generally high molar extinction coefficient, and to the medium to high light and wet fastness properties\textsuperscript{67}. The azo pyridone dyes give bright hues and are therefore of investigative interest\textsuperscript{68}.

Rangnekar and Kanhere\textsuperscript{69} have reported bisazo disperse dyes (34), giving yellow to red shades. 2-pyridone derivatives are also used in preparation of various bisazo disperse dyes (35-36)\textsuperscript{70}. 
Some heterocyclic compounds are also reported as pyridone dyes. Here 5-amino-2-pyridone is used as diazonium salt and couple with heterocyclic ring (37) and (38)\textsuperscript{71}.

The syntheses of phthalimide based pyridone azo disperse dyes (39) and their spectral properties were investigated. The synthesized dyes developed the color of yellow to violet and the N-substitution of the phthalimide gave a bathochromic effect on the color change. Most of the synthesized dyes exhibit negative solvatochromism, so that the absorption band of dyes moves toward shorter wavelengths as the polarity of the solvent increases\textsuperscript{72}.  

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Two pyridone-based disperse yellow dyes (40) in the hydrazone form having different ethyl and methyl substituents have been structurally characterized and compared. After metal-ion complexation (41) with Ni\(^{2+}\) and Cu\(^{2+}\) ions, conformational interconversions between azo/hydrazone and cis/trans isomers have been achieved, where the azo ligands show bidentate, tridentate and tetradebate coordination modes\(^{73}\).

A novel protocol (42) for the rapid synthesis of pyridone colorants under controlled microwave irradiation in a dedicated reactor is described. Short reaction times, high yields and versatility for different substrates are the advantages of this method\(^{74}\).

Where, \(R_1, R_2, R_3, R_4 = H, Me., Ph., br., NO_2, I\)
The synthesis of a series of 3-(p-substituted phenylazo)-6-pyridone dyes (43) which is suitable for the dyeing of polyester fabrics, is described. Visible absorption spectra of the dyes were examined in various solvents and the compounds in solution exhibited hydrazone-common anion equilibrium. The colour parameters of the dyed fabrics were measured. All synthesized compounds shows excellent exhaustion and fastness properties. The remarkable degree of levelness and brightness after washing is indicative of good penetration and excellent affinity of these dyes for the polyester fabric.

![Diagram of compound 43]

Where, X = H, SO$_3$H, COOH, CH$_3$O, Cl, OH

Absorption spectra of 5-(4-substituted arylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridones (44) have been recorded. The effects of substituents on the absorption spectra of investigated compounds are interpreted by correlation of absorption frequencies with simple Hammett equation. The effects of solvent polarity and solvent/solute hydrogen bonding interactions are analyzed. The azo-hydrazone tautomeric equilibration is found to depend upon substituents as well as on solvents.

![Diagram of compound 44]

Where, X = OH, OCH$_3$, CH$_3$, C$_2$H$_5$, H, Cl, Br, I, COOH, NO$_2$
1-ethyl-3-cyano-6-hydroxy-4-methyl - 5 - amino-2-pyridone was coupled with 1, 3, 3-trimethyl-2-metheneindoline, 1-phenyl-3-methyl-5-pyrazolone, 1-ethyl-3-cyano-6-hydroxy-4-methyl-2-pyridone and barbituric acid and gives (37), (38), (45) and (46), respectively. The absorption properties of these new azo dyes were investigated in various solvents and the mixture solvent of chloroform/DMSO with different volume ratios.

5-amino-3-methyl-4-heteroarylazo-1H-pyrazoles coupling with 3-cyano-6-hydroxy-4-methyl-2-pyridone and 3-methyl-1H-pyrazole-5-one. The novel dyes (47) were characterized by elemental analysis and spectral methods and the solvatochromic behaviour of the dyes in various solvents was evaluated. Substituent, acid and base effects on the visible absorption maxima of the dyes were also reported.

Huang W. and Qian H. synthesized azo dye molecule (48), C.I. Disperse Yellow 114, with a 1-methyl-5-cyano-2-hydroxy-4-methyl-6-pyridone component. The dye crystallizes in the hydrazone form.
The catalytic fading of combination dyeing on polyester fabric of pyridone-azo yellow disperse dyes (49) imparted by C.I. Disperse Blue 165 as a result of exposure to a carbon arch in air was analyzed in terms of reactivity ($k_0$). Disperse dyes with excellent light fastness on polyester exhibit low values of both $f$ and $k_0$. The $f$ values observed for the combination dyeing did not show simple additivity.$^{80}$

New antipyrinylazo dyes (50) were prepared by diazocoupling of 4-antipyrinyl diazonium chloride with a variety of coupling components e.g. thiazole, thiophene, pyridone, and pyrazole moieties. These dyes were applied as disperse dyes for dyeing polyester fabrics and their fastness properties were evaluated.$^{81}$

Synthesized azo pyridone dye (5-(4-sulpho phenylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridone) shows photocatalytic degradation in
aqueous solutions. Degradation of the dye was enhanced by hydrogen peroxide, but it was inhibited by ethanol. The influence of temperature was studied, and the energy of activation was determined. In addition, photocatalytic degradation of simulated dyehouse effluents, containing tested azo pyridone dye and associated auxiliary chemicals were investigated.

![Image](attachment:structure.png)

1.2 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 required polarity enables to get blue shades from structures such as \((52-53)\).

![Image](attachment:structure1.png)

![Image](attachment:structure2.png)

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 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 (54) or 2-amino-5-nitrothiazole (55) with coupling component (56) are blue to greenish blue.

Consequently dyes with heterocyclic diazo components have received much attention since they offer high tintorial power, excellent brightness and fastness and commercially competitive with more expensive with more anthraquinone dyes. In this context, literature survey has featured considerable growth in the research of synthesis, properties and application of heteroaryl azo dyes in the last two decades.

1.3 Dyeing of fiber with disperse dyes

Disperse dyes emerge as a fairly common class of dyes for application to the majority of synthetic fibers. Disperse dyes commonly used to dye polyester which are nonionic and dyed 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. Deep shades and good fastness properties on polyester can be achieved by using disperse dyes in presences of carriers, or high
temperature dyeing techniques. 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. These disperse dyes are mainly azo dyes. Azo dyes have heterocyclic intermediates either as diazonium components and coupling components for 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 application methods and provide needed improvement in fastness properties. Six different methods have been developed:

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 exhaustion and 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 2100°C for 30 seconds, is an important development.
5. Solvent dyeing methods are available, but are not popular.
6. Printing and dyeing processes have been developed for polyester blends using specialist dyes and application techniques.

1.4 Research gap about pyridone based bisazo heterocyclic dyes

Azo dyes based on heterocyclic amines have been developed and the resultant dyes give higher tintorial strength and brighter dyeing than those derived from aniline based diazo components. For instance amino substituted thiazole compounds afford highly electronegative diazo compounds and consequently provide a pronounced bathochromic effect. Although, many patents and papers describe the synthesis and dyeing properties of monoazo heterocyclic dyes, very few comparable investigations have been made with bisazo heterocyclic dyes as specially with pyridone moiety. We
have previously reported the synthesis of various heteroaryl azo dyes. Continuing our earlier studies designed to prepare new bisazo heterocyclic dyes for dyeing polyester fabric.

1.5 Objectives

In view of above review, the prime objectives of the present thesis are

[1] Synthesis of Bis-heteroaryl and tris-heteroaryl Bisazo dyes by using monoazo pyridone dyes and various aromatic and heterocyclic amines, respectively.


1.6 Present work

Section I of thesis deals with synthesis and characterization of pyridone based heterocyclic bisazo dyes.

Chapter-2 of the thesis comprises into two sections.
Section-A gives details about techniques used for characterization.
Section-B deals with the synthesis of novel bisazo bis heteroaryl dyes. Elemental analysis, FT–IR, $^1$H NMR, $^{13}$C NMR, DEPT and UV spectroscopic techniques were used to characterize the structures and summarized solvatochromic behavior for synthesized novel dyes.

Chapter-3 deals with the preparation of new bisazo tris heteroaryl disperse dyes. Elemental analysis, FT–IR, $^1$H NMR, $^{13}$C NMR, DEPT and UV spectroscopic techniques were used to characterize the structures and summarized solvatochromic behavior for synthesized novel dyes.

Chapter-4 deals with the study of dyeing properties of bisazo disperse dyes on polyester fabric. The applicability of these new bisazo disperse dyes have been evaluated by exhaustion and fixation studies of dye as well as by estimation of the fastness properties such as wash fastness,
light fastness, rubbing fastness, sublimation fastness and perspiration fastness of dyed fabrics.

\[
\begin{align*}
R & \quad \text{Nitrosyl sulphuric acid} \\
& \quad 0-5^\circ C
\end{align*}
\]

where, \( R_1 \) = -CH\(_2\)CH\(_3\), -CH\(_2\)\(_2\)CH\(_2\)CH\(_3\), -(CH\(_2\)\(_2\)CH\(_2\))OCH\(_3\)

\( R_2 \) = a)-H, b)-NO\(_2\), c)-COOH, d)-OH,
  e)-CH\(_3\), f)-OCH\(_3\), g)-Cl, h)-Br

where, \( R = -NO_2, -Cl \)

\( \text{Ar} = \text{various derivatives of 2-aminothiazol,} \)
= \text{various derivatives of 2-aminothiadiazole,}
= \text{various derivatives of 2-aminotriazole}

**Synthetic route for heterocyclic bisazo dyes**
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