INTRODUCTION

Reactive dyes are coloured compounds which contain one or two groups capable of forming covalent bond between a carbon or phosphorous atom of the dye ion or molecule and an oxygen, nitrogen or sulphur atom of a hydroxyl, an amino or a mercapto group, respectively of the substrate. Such covalent bonds are formed with the hydroxyl groups of cellulosic fibres, with the amino, hydroxyl and mercapto groups of protein fibres and with the amino groups of polyamides [1]. In general, reactive dyes are the only textile colourants designed to bond covalently with the substrate on application. They are used for the dyeing and printing of cellulose and to a lesser extent polyamide fibres. They are valued for their brilliance and variety of hue, versatility and high wet fastness profiles. The possibility of forming covalent bond between dyes and fibres had long been attractive to dye chemists, since attachment by physical adsorption and by mechanical obstruction had the disadvantage of either low wash fastness or high cost [2, 3]. It was anticipated that the covalent attachment of the dye molecules to the fibre would produce very high fastness because covalent bonds were the strongest known binding forces between molecules [4, 5].

It was the first time that dyeing has been done by chemical reaction between the dye and the fibre, enabling one to get design of bright, attractive shades of sufficient fastness with considerable comfort of dyeing. It can easily be understood that dyes with two reactive groups give a higher fixation yield than dyes with one reactive group [6,7], for it one of the two dye fibre bond is hydrolysed and one is still left for fixation [8,9]. These dyes are used on higher value clothes which are normally mercerized [10]. Rouette employed the bifunctional reactive dye for safe dyeing of intimate colours on severely impairment carbonized wool [11]. The presence of 1,3,5-triazine structure in the dye molecule improves their dyeing ability and possibility for application[12].

The demand of reactive dyes rapid increase due to the excellent characteristics such as brilliant shades, excellent wet fastness of dyeing and simple dyeing operations which have increasingly been accepted within the industry. However, with the growth in the usage of reactive dyes, additional properties have been demanded by dye works
and apparel manufactures [13-16] in particular high fixation in exhaustion dyeing and high fastness to chlorine perspiration, light and washing in the presence of peroxides.

The first commercial reactive dyes for cellulose were developed by Rattee and Stephen and marketed by ICI in 1956 under the trade name Procion M [17-22]. These dyes were introduced for the production of fast bright shades on cellulosics fibres using continuous dyeing methods. Reactive dyes, the newest addition of existing dyes are the centre of attraction in dyestuff research [23,24]. Several new reactive system have been introduced from time to time, which covers the subject of innumerable patents and publications [25-27]. Reactive dyes have also been developed for application on protein and polyamide fibres. In addition, investigations into the development of reactive dyes for polyester and polypropylene fibres have been demonstrated to the level of technical possibility but such dyes are not yet of commercial interest [28,29].

The major factor contributing to the long delay in producing the first reactive dye for cellulose was the belief that cellulose was a relatively inert substrate and that conditions required to effect a chemical reaction would cause serious fibre degradation [30,31]. Therefore, in early studies dyestuff chemists were led astray in thinking that they needed to convert cellulose to the more reactive soda cellulose to make fibre reactivity possible [32,33]. Yet a large number of reactive dyes with varieties of reactive groups were eventually developed.

The various aspects of s-triazine dyes are published by several workers [34]. s-Triazine based chemicals have been applied widely in manufacture of polymers, dyes, explosives, pesticides and commodity chemicals [35]. As consequence, theoretical and experimental studies on these chemicals have widely carried out [36,37] with the result that s-triazine ring is known as an important conjugated heterocycle whose electronics properties are different from those of benzene due to the alternate replacement of –CH= groups by nitrogen atoms [38].

The most important heterocycles are those in which five or six membered rings and may be fused to other rings, especially a benzene ring. Nitrogen, sulphur and to a lesser extent oxygen are the most frequently encountered hetero atoms. e.g. Pyrazolones [39] are used as coupling components since they couple readily at the 4-position under alkaline conditions to give important azo dyes in the yellow
shade. In recent years, heterocyclic amines such as derivatives of azo dyes from amino heterocycles like quinoline [40], isoquinoline [41], cinnoline [42], quinoxaline [43], and quinazoline [44] have been reported.

DEVELOPMENTS:

The first industrially important reactive dye systems were developed for wool and took advantage of the chloroacetylamino [45] and the chloroethanesulphonyl groups [46]. Vinylsulphonyl and 2-sulpho oxy ethanesulphonyl groups were found to be applicable to both wool and cellulose. Heyna and Schumacher patented some of the first dyes of this type in the 1940s [47,48] and vinylsulphone dyes continue to be of great importance.

Rattee and Stephen were working on the problem of reactive dyes for wool. Stephen, who had previously worked [49] on dichlorotriazinyl derivatives in another connection and had been impressed by their high reactivity, prepared several dyes containing 2,4-dichloro-s-triazine-6-amino groups of assessment [50] in the hope that almost complete reaction with the wool fibre might be attained. Rattee and Stephen of ICI, whose initiative was subsequently recognized in 1959 by a joint award of the Gold Medal of the Society of Dyers and Colourists for the Invention and Development of the first practical system of colouring cellulose fibre reactive dyes [21].

Reactive dyes bearing two mono chloro triazinyl groups occupy an important place in cellulosic dyeing. The first range of the dyes based on this general concept, the procion H-E range, was launched by ICI in the late 1960s [51] and many of the original product continue to be widely manufactured over the intervening years, new products have been introduced based on this concepts, but with chloro, fluoro or nicotinyl leaving groups. These include Kayacelon React (Nippon Kayaku) and Procion H-EXL (BASF), Cibacron LS (Ciba) and Drimarene XN (Clariant).

Cross and Bevan first succeeded in fixing dyes covalently on to cellulose fibres [52], but their multistep process was too complicated for practical application. Early work by Schroeter with sulphonyl chloride based dyes was unsuccessful [53] but Gunther later did succeed in fixing derivatives of isotoic anhydride on to the cellulose fibres [54].
CONSTITUTION OF REACTIVE DYES:

In principle, a reactive dye should contain a leaving group (X) which can undergo nucleophilic displacement by hydroxyl group of cellulose in the presence of aqueous alkali

\[(\text{Dye} - \text{X} + \text{Cell} - \text{O}^- \rightarrow \text{Dye} - \text{O} - \text{Cell} + \text{X}^-)\] or

an activated \(-\text{C} = \text{C}-\) bond which is able to add to a hydroxyl group of cellulose

\[(-\text{CH} = \text{CH}_2 + \text{Cell} - \text{OH} \rightarrow -\text{CH}_2 - \text{CH}_2 - \text{O} - \text{Cell}).\]

Reactive dyes are the only textile colouration products designed to furnish covalent bonds between dye and substrate during dyeing. Although many different reactions can be used for fixation, two main types are exploited commercially, i.e. hetero aromatic nucleophilic substitution and addition to an activated alkane [55-57].

Thus, the majority of reactive dyes can be distinguished into two categories by their reaction modes as:

(i) Nucleophilic addition-elimination dyes:

\[\text{XN} = \text{C} \begin{array}{c} \text{Y} \\ \text{N} \end{array} \text{X} \leftrightarrow \text{XN} = \text{C} \begin{array}{c} \text{Y} \\ \text{N} \end{array} \text{X} \quad \text{X}^- \]

(ii) Nucleophilic addition dyes:

\[-\text{CH} = \text{CH}_2 \leftrightarrow \text{CH} = \text{CH}_2 \text{Y} \leftrightarrow \text{CH}_2 \text{CH}_2 \text{Y} \leftrightarrow \text{CH}_2 \text{CH}_2 \text{Y}\]

The general formula of a reactive dye is given as,

\[a - c - b - R\]

Where, ‘a’ is water-solubilizing group. Generally, \(-\text{SO}_3\text{Na}\) and \(-\text{COONa}\) groups are used as a water-solubilizing group; ‘b’ is a bridging group which links together chromophoric ‘c’ and reactive ‘R’ systems. The commonly used bridging groups are \(-\text{NH}-\), \(-\text{N(CH}_3)-\), and \(-\text{CH}_2\text{O}-\) etc. The bridge unit affects to a great extent, the reactivity of the dye and the tendency of the corresponding dyeing to hydrolyse.
‘R’ is a reactive group. The dye-fibre compound may have the properties of an ester or ether, the precise nature and stability of the dye fibre bond will depend on the reactive group.

Chromophoric system ‘c’ is mainly responsible for the colour of the dye. Various types of shade can be obtained by changing the chromophoric system. From the large number of suggested chromophoric system azo, antraquinone and phthalocyanine derivatives have achieved greatest economical importance up to present date. Dyestuff of these groups from the hard core of all commercial reactive dyestuff ranges. The widest range of shades is covered by the azo compounds, which comprise practically every shade from greenish yellow to black. Brilliant blue and green shades with high fastness to light are mainly from anthraquinone derivatives, while sulphonic acids of copper and nickel phthalocyanine are used to produce turquoise shades and in combination with yellow dyestuff to synthesise bright green shades.
CLASSIFICATION OF REACTIVE DYES:
Reactive dyes can be classified into different groups as follows:

MAJOR COMMERCIAL TYPES OF REACTIVE DYES FOR CELLULOSE

<table>
<thead>
<tr>
<th>Structure</th>
<th>Commercial Name</th>
<th>Firm</th>
<th>Year of Introduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D)–HN–N=N–N=Cl</td>
<td>Procion</td>
<td>ICI</td>
<td>1956</td>
</tr>
<tr>
<td>(D)–HN–N=N–N=Cl</td>
<td>Procion H</td>
<td>ICI</td>
<td>1957</td>
</tr>
<tr>
<td></td>
<td>Cibacron</td>
<td>CIBA</td>
<td>1957</td>
</tr>
<tr>
<td>(D)–SO₂–CH₂–CH₂–OSO₃Na</td>
<td>Remazol</td>
<td>Hoechst</td>
<td>1958</td>
</tr>
<tr>
<td>(D)–HN–N=S=SO₂CH₃</td>
<td>Levafix P</td>
<td>Bayer</td>
<td>1966</td>
</tr>
<tr>
<td></td>
<td>Primazin P</td>
<td>BASF</td>
<td>1964</td>
</tr>
</tbody>
</table>
### MAJOR COMMERCIAL TYPES OF REACTIVE DYES FOR WOOL AND POLYAMIDES

<table>
<thead>
<tr>
<th>Structure</th>
<th>Commercial Name</th>
<th>Firm</th>
<th>Year of Introduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2-Metal Complex  &lt;br&gt; Dye — NH — OC — CH=CH₂  &lt;br&gt; ![Image](1:2-Metal Complex.png)</td>
<td>Procilan</td>
<td>ICI</td>
<td>1964</td>
</tr>
<tr>
<td>&lt;br&gt; (D) — NH — OC — C = CH₂  &lt;br&gt; <img src="D.png" alt="Image" /></td>
<td>Lanasol</td>
<td>CIBA</td>
<td>1966</td>
</tr>
<tr>
<td>&lt;br&gt; (D) — HN —  &lt;br&gt; <img src="D.png" alt="Image" /></td>
<td>Verofix  &lt;br&gt; Drimalan F  &lt;br&gt; <img src="Verofix.png" alt="Image" /></td>
<td>Bayer  &lt;br&gt; Sandoz</td>
<td>1970</td>
</tr>
</tbody>
</table>

### VARIOUS REACTIVE SYSTEMS:

Reactive systems, in general, can be classified as aliphatic, aromatic and heterocyclic reactive system as follows.

[A] **Aliphatic Carrier Systems of Labile Groups:**

(a) **Substituted Alkane-Mono Carboxylic Acid Amides:**

The dyeing of cellulosic textiles with dyestuffs containing chloroacetylamino groups (I) was first described by BASF [58], and later also by other firms. The fixation yields of these chloroacetylamino reactive dyestuffs are also not particularly high on cellulosic fibres.

![Image](I.png)
In a BASF patent [59] relating to β-sulphonylpropionamide dyestuffs (II), sulphonyl group is described and claimed in anthraquinone, azo and phthalocyanine dyes.

\[
\text{CIBA [60] described wool-reactive dyes containing β-chloro propionylamino groups (III) and recognized the suitabilities of β-chloro propionylamino dyestuffs, which are in most cases freely water-soluble and possess little affinity for the continuous dyeing and printing cellulosic fibres [61].}
\]

\[
\text{α, β - Dihalopropionamides (IV) were developed by CIBA [62] in cellulose reactive dyes. The use of dichloro or dibromo propionic acid [63] is claimed in a number of new dyes. Among other substituted aliphatic carboxylic acid, amides and substituted isobutyric acid amides [64] are claimed as new reactive components.}
\]
(b) **Substituted Aliphatic Ketones:**

The stability of dyestuffs containing chloromethyl or β-chloroethyl aryl ketone groups (V) for the dyeing of cellulose in the presence of alkali was recognized by BASF and General Aniline [65].

\[
\text{Cl}(\text{CH}_2)n\text{C} \quad \text{N} = \text{N} \quad \text{CH}_3
\]

\[
\text{HO} \quad \text{N} \quad \text{N}
\]

\[
\text{SO}_3\text{H}
\]

\[n = 1, 2 \quad (V)\]

(c) **Substituted Alkane-Monocarboxylates:**

This new reactive dyestuffs group (VI) was discovered by General Aniline and Film Corporation [66]. In such dyes saponification of propionic ester, bond takes place resulting in the fixation in good yield and fastness to washing.

\[
\text{O} \quad \text{NH}_2 \quad \text{SO}_3\text{H}
\]

\[
\text{CH}_2\text{O} \quad \text{C} \quad \text{CH}_2\text{CH}_2\text{CH}_2\text{X}
\]

\[
\text{CH}_2\text{O} \quad \text{C} \quad \text{CH}_2\text{CH}_2\text{CH}_2\text{X}
\]

\[(VI)\]

(d) **Substituted Cycloalkane Carboxamide:**

From ethylene tetra fluoride and acrylonitrile or 1-cyano-butadine or their derivatives, fluoro cyclobutane carboxamides (VII) are useful reactive dyestuff groups. Farbwerke Hoechst and other firms [67] have claimed number of patents related to this group.
(e) β - Substituted Ethyl Sulphone - Vinyl Sulphones:

The following reactive systems are frequently referred to as ‘Vinyl Sulphones’ to simplify matters, though strictly speaking they are Vinyl sulphone intermediates.

For this reason, the majority of papers and patent specifications refer to a multitude of β-substituents (X), which are quite easy to eliminate, e.g. X = -Cl. Reactive dyes containing β-haloethyl sulphone groups are recommended by CIBA [68] for the dyeing of cellulose. Generally β-substituents X= -Cl, -N(Alkyl)$_2$, -SO$_3$H, -OPH$_2$O$_3$, but primarily -OSO$_3$H is used. In the case of azo dyes, the vinyl sulphone group is usually substituted directly into the aryl nucleus of the diazo component or that of the coupling component. In a number of patents, however bridges are included e.g. –NH–, –(CH$_2$)$_n$–, –CONR(CH$_2$)$_n$–, –SO$_2$NRAryl–, –CONR Aryl– and –NRSO$_2$Aryl– between the aryl nucleus and the vinylsulphone group. In this connection, references have been made to a large number of patents primarily from Farbwerke Hoechst, as well Sumitomo and other firms [69,70] covering this reactive group (VIII & IX).
In some reviews, attention is focused on the development of vinyl sulphone dyes [71] and their general fields of applications.

(f) Alkene Monocarboxamides:

Reactive dyes with β-chloropropionylamide groups containing acrylamide are fairly slow in their reaction. They are less suitable for the dyeing of cellulosic materials than for pad dyeing processes and textile printing. The crotonamide group is even less reactive.

(g) β - Substituted Ethylamine Derivatives:

In 1956, dyestuffs containing β-haloethylamines group for dyeing cellulosic materials was described by BASF [72]. The N, N'-bis-(β-chloro-ethyl)-hydrazide group (X) claimed by Sandoz is interesting from chemistry point of view. Thus all ethylamine derivatives, containing a group in the β-position, which is capable of splitting off together with the bonding electron pair under alkaline medium, have been mentioned as reactive groups used in reactive dyes for the dyeing of cellulose, nylon and wool.

![Chemical Structure](image)

(X)

(h) Epoxide Derivatives and Their Precursors:

The group (a) and its precursor (b) are nearly always mentioned together. Water-soluble reactive dyes of this type give dyeing with very good wet fastness properties.
(i) β - Substituted Ethylamides of Sulphonic Acids:

ICI [73] recognized that the water-soluble dye (XI) containing N-β-halo ethyl sulphonamide groups are fixed on cellulosic fibres from aqueous alkaline medium shades which possess excellent wet-fastness properties.

![Chemical Structure (XI)]

[B] Aromatic Carrier Systems:

Due to equivalence of the group $\equiv N\equiv$ and $\equiv O\equiv N\equiv C\equiv$ with regard to the activation of halogen atoms in the ortho or para position in hetroaromatic or aromatic rings, the aromatic carrier systems are rarely used. The virtual absence of papers on the use of well-known aromatic carrier systems shows that they are of little practical importance. One of the interesting systems [74] is given below (XII).

![Chemical Structure (XII)]

[C] Heterocyclic Carrier Systems:

(a) Pyridine Derivatives:

Halogen substituents attached to pyridine or quinoline systems are not sufficiently reactive to form covalent bonds with cellulose under normal dyeing or printing conditions unless suitably situated electron-attracting groups are also present in the ring to give enhanced reactivity. By condensation of amino dyestuffs with 3, 5-activated 2, 6-dichloropyridine [75] derivatives, easily fixed reactive dyes (XIII) are obtained.
(b) Pyridazone derivatives:

This reactive group has been achieved technical importance in reaction, the 6-pyridazone substituted on nitrogen atom 1 is not an aromatic nitrogen heterocyclic; its 4, 5-dihalo derivatives react in the 4-position as vinylogous carbonyl halides.

(c) Pyridazine Derivatives:

Dyestuffs containing chloropyridazine groups [76] are suitable for the printing and continuous dyeing of cellulosic fibres with subsequent fixation in dry heat or in steam. Tetrachloropyridazine condensed in an aqueous alcoholic medium with 1,3-diamino benzene-4-sulfonic acid, after diazotisation and coupling gives the following dyestuff (XIV)
(d) Pyrimidine Derivatives:

Pyrimidine is the most important heterocyclic carrier system.

**Reactive Dyes containing a Chloropyrimidine Nucleus:**

a) Dichloropyrimidine type

![Dichloropyrimidine structure]

(b) Trichloropyrimidine type

Reaction Drimarene Z

![Trichloropyrimidine structure]

**Reactive Dyes Containing a Cyanuric chloride Nucleus:**

Cyanuric chloride contains three labile chlorine atoms which can be replaced in succession to an amine salt or a hydroxyl compound. A simple dye containing a cyanuric chloride can be represented as follows:

(a) Procion H

Cibacron

![Cyanuric chloride structure]

Monochlorotriazine reactive dyes

X = Aromatic or Aliphatic amine or dye with a free amino group attached to the chlorine or heterocyclic residue.

(b) Procion M

![Dichlorotriazine structure]
1,2,4-Triazine Derivatives:

1,2,4-Triazine are suitable as reactive compounds. Finally powdered 3,5-dichloro-1,2,4-triazine condense with the appropriate amino azo dyestuff in aqueous solution at 0-5 °C and pH 4.5-6.0 forming a reactive dyestuff, the constitution of which (substitutions position on 1,2,4-triazine) is not exactly known.

Phthalazine Derivatives:

Dyestuff with1, 4-dichlorophthalazine-6-carbonyl chloride, reactive components are extremely suitable for textile printing and continuous dyeing. Bayer [77] recognized the value of this dyestuffs group under the name Elisiane dyestuffs (XV).

![Elisiane Brilliant Red B (XV)](image)

Azo Reactive Dyes:

This specifically important reactive principal was developed by Bayer [78], Dupont [79], CIBA [80] and Francolor [81]. Commercial products on this basis are Levafix E dyestuffs and the Cavalite dyestuffs (XVI).

![Levafix Brilliant Red E-2B (XVI)](image)

ICI [82] discovered the cyanuric bromide is also suitable for the synthesis of reactive dyestuff (XVII).

![Cavallite Red Y](image)
Ciba-Geigy synthesised [83] a reactive azo dyes (XVIII) for silk, leather, wool, polyamide, fibers, polyurathanes, rayon, cotton and cellulose.

ICI [84] had also produced most commercial reactive ranges in the field of Brilliant Red dye (XIX) is found in the coupling products of 1-amino-8-naphthol-3,6-disulphonic acid.

ICI [85,86] also patented the dyestuff Procion Yellow M-RS (XX) as well as Procion Brilliant Orange M-FS (XXI) in the year 1954.
CIBA [87] synthesized fibre reactive azonaphtholsulfonic acid dyes (XXII) gave a Reddish Brown dye for cotton.

![Image of compound XXII]

Where, $R = -\text{Cl, -NH}_2$

Jin et al. [88] have synthesized scarlet dyes (XXIII) for cotton fabrics.

![Image of compound XXIII]

Where, $R = -\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$

Mistry P. M. and Taylor J. A [89] have synthesized navy blue reactive azo dyes (XXIV) for cotton. The compounds are characterized by good strength and caliber to build up exhaust and pad-batch dyeing to good depths of shade, producing good coloured and fastness properties.

![Image of compound XXIV]

Herd et al. [90] have synthesized reactive dyes (XXV) containing a halopyrimidinyl anchor group useful for the high colour yield dyeing or printing of hydroxyl or amide group containing fabrics in fast bluish red shade on cotton.
Oesterlein F. and Seitz K. [91] have synthesized reactive disazo dye having structure (XXVI) gave greenish blue dye for cotton.

Where, $R = \text{Et, Me.}$

$R_1 = \text{H, NH}_2, \text{SO}_3\text{H.}$

Mokhtari et al. [92] have synthesized trisazo heterobifunctional reactive dyes (XXVII) gave variety of shade on cotton and good fastness properties.

Where, $Z= $

$X = -\text{CH}_3, -\text{H}, -\text{SO}_3\text{Na}.$

$Y = -\text{CH}_3, -\text{OCH}_3, -\text{OC}_2\text{H}_5$
Gillingham E. L. and Lewis D. M. and Srikulkit K. [93] have synthesised triazinylamino alkylphosphonate reactive dyes (XXVIII) for cotton fabric.

Mousa A. A. [94] has synthesized polyfunctional reactive dyes (XXIX) containing bis (monochloro triazine/ sulphatoethyl sulphone) reactive system showed good dyeing property on silk. The twinned MCT/SES reactive system deliver relatively high fixation efficiency even at low salt/temp condition.

Where, $R =$

![Image of molecular structure](image)

Paluszkiewicz J. and Czajkowski W. [95] have synthesized bifunctional reactive dyes (XXX) with quinolino-s-triazine groups, and their dyeing properties of cotton fabrics were determined.
Tzikas Athanassios and Crotese Bruno [96] have synthesized reactive diazo dyes (XXXI) gave fast yellow shades on cotton.

Where, \( A = \text{sulphoaryl.} \)

\[
\begin{align*}
R_1, R_2 &= \text{H, optionally substituted C}_{1-4} \text{ alkyl.} \\
R_3, R_4 &= \text{H, C}_{1-4} \text{ alkyl, C}_{1-4} \text{ alkoxy, halogen, carboxy, sulfo.} \\
R_5, R_6 &= \text{H, C}_{1-6} \text{ alkyl, C}_{1-4} \text{ alkoxy, halogen, nitro, C}_{2-4} \text{ alkanoylamino, benzoyl amino, ureido, carboxy, sulfo.} \\
X &= \text{halogen.} \\
ZY &= \text{vinyl sulphone generating group.}
\end{align*}
\]

Petrova-Miladinova P. and Konstantinova T. N. [97] have synthesized reactive triazine azodyes (XXXII) containing tertamethyl piperidine (TMP) piece. The dyes co-polymerized with acryl amide and acrylonitrile and the co-polymer with an intense orange colour that is stable to solvent extraction.

Where, \( A_1 = -\text{NH}_2, A_2 = -\text{Cl} \)
Yung – Jian Gau, Philip Duncan and Taylor John G. [98] have synthesized blue reactive azo dyestuff (XXXIII).

Where, $R_1, R_2 = H, C_{1-4}$ alkyl, $C_{1-4}$ epoxy, Sulphonic acid.

$X = \text{halogen.}$

$X_1, X_2 = \text{OH, NH}_2.$

$Y = \text{SO}_2\text{CH}_2: \text{CH}_2, \text{SO}_2\text{C}_2\text{H}_4\text{W}; \text{W} = \text{OSO}_3\text{H}.$

$Z = \text{CHTCH}_2\text{T, CT} : \text{CH}_2; \text{T} = \text{halogen.}$

Akerman D., Giannoulis A. I., Phillips D. A. S., Taylor J. A. [99] have synthesized azo/hydrazo dyes (XXXIV) based on H- acid, with superior resistance to oxidative bleach fading.

Where, $X = \text{H, Cl, Br}$

$Y = \text{H, Cl, Br}$

$\text{SES} = \text{Sulfato Ethane Sulphonyl.}$

Pingzhong Chu and his co-workers have [100] synthesized monoazo reactive brown dyes (XXXV) gave good light fastness, perspiration resistance and soaping resistance. They can be applied to dip dyeing, pad dyeing, jig dyeing and continuous pad dyeing of cotton, rayon and hemp textiles.
Where, $R_1 = H, \text{Me, Methoxy or Sulfonic group.}$

$R_2 = H, \text{Me, Methoxy.}$

$R_3 = H, \text{Sulfonic gr. or } -\text{COOH.}$

$Z = -\text{SO}_2\text{Y (on the m-position or p-position of amino group)}$

$M = H \text{or alkali metal.}$

Patel et al. [101] have also synthesized bisazo reactive dyes (XXXVI) by coupling of diazotised 4,4'-diaminobenzanilide with various cyanurated coupling components. Their dyeing performance on silk, wool and cotton fibres has been assessed. The dyed fibre showed fair to very good light fastness and very good to excellent washing and rubbing fastness.

Where, $R =$ various cyanurated coupling components.

Patel Bhavesh M. and Patel Saurabh K. [102] have synthesized bisazo reactive dyes (XXXVII) gave a wide range of violet to red shades on cotton fibre.

Where, $R =$ H-acid, N-benzoyl H-acid, N-methyl J-acid, Peri acid and R-acid.

Pasha Khalid and Taylor John A. [103] have synthesized two heterobi-functional reactive dyes (XXXVIII, XXXIX). Their dyeing properties including exhaustion, colour strength on fabric, fixation and wash fastness were compared with major products.
Patel et al. [104] have synthesized bisazo dichloro-s-triazinyl reactive dyes (XL) bearing 1,3,4-oxadiazole molecule by coupling of tetrazotized 2,5-bis(4-amino phenyl)-1,3,4-oxadiazole with various cyanurated coupling components. The exhaustion, fixation and fastness properties of the dyed fabric were evaluated. The dyes showed moderate to very good light and good to excellent washing and rubbing fastness properties.

Where, \( R \) = various cyanurated coupling components.

Saeed Aamer and Shabir Ghulam [105] have synthesized and characterised high wash fastness novel azo reactive dyes (XLI) including aromatic bridged diamines using different substituted bis anilines.
Where, \( \text{ABC} \) = different substituted bis anilines.

Patel et al. [106] have also synthesized bisazo reactive dyes (XLII) by coupling of diazotised 4,4'-methylene-bis-anthranilic acid with various anilino cyanurated coupling components. Their dyeing performance on viscose rayon, wool and silk fibres has been assessed. The dyed fibre showed fair to very good fastness to light, washing and rubbing fastness.

\[
\text{HOOC} \quad R \quad \text{N} \quad \text{N} \quad \text{CH}_2 \quad \text{N} \quad \text{N} \quad \text{R} \quad \text{COOH}
\]

Where, \( R \) = various anilino cyanurated coupling components.

Mehta et al. [107] have synthesized cold brand bisazo reactive dyes (XLIII) for silk, wool and cotton fibres. Exhaustion, fixation and fastness properties of these dyes were also reported.

\[
R \quad \text{N} \quad \text{N} \quad \text{CH}_2 \quad \text{N} \quad \text{N} \quad \text{R}
\]

Where, \( R \) = various cyanurated coupling components.
Patel et al. [108] have also synthesized hot brand bisazo reactive dyes (XLIV). These dyes were applied on silk, wool and cotton fibres. The fastness properties, exhaustion and fixation value were also been studied.

![Chemical structure of XLIV](image)

Where, \( R = \text{various m-nitro anilino cyanurated coupling components.} \)

Patel et al. [109] have also synthesized hot brand reactive dyes (XLV) by coupling tetrazotized 4,4′–methylene bis 2,5–dichloroaniline with various m-toluidino cyanurated coupling component for silk, wool and cotton fabrics. The fastness properties of dyes gave very good order.

![Chemical structure of XLV](image)

Where, \( R = \text{various m-nitro anilino cyanurated coupling components.} \)

Patel Bhavesh M. and Patel Saurabh K. [110] have synthesised novel bisazo reactive dyes (XLVI). The fastness properties, exhaustion and fixation data were also been studied.

![Chemical structure of XLVI](image)

Where, \( R = \text{various cyanurated coupling components.} \)
Patel et al. [111] have also synthesized hot brand bisazo reactive dyes (XLVII). These dyes were applied on silk, wool and cotton fibres. The percentage dye bath exhaustion of different fibres was judicious good and acceptable. The dyes exhibited high levels of light, washing and rubbing fastness.

![Image](image_url)

(XLVII)

Where, \( R \) = various 5-sulfo anthranilo cyanurated coupling components.

Patel Divyesh R and his co-workers [112] have synthesized acid dyes (XLVIII) by coupling of diazotized 4-morphollino-6-amino quinazoline with various coupling components. These dyes were applied on silk and wool. Their colorimetric data (\( L^*, a^*, b^*, H^* \) and \( C^* \)) have also been studied.

![Image](image_url)

(XLVIII)

Where, \( R \) = H-acid, J-acid, N-methyl J-acid, N-phenyl J-acid, Gamaa acid, N-methyl gamma-acid, Chicago acid and K-acid.

Parekh N. M. and Mahera K. C. [113] have synthesized benzoquinoline based hot brand monoazo reactive dyes (XLIX). Their dyeing performances on various fibres have been assessed. Their spectral properties and colorimetric data have also been studied. These dyes gave good fastness properties on cotton silk and wool fibres.

![Image](image_url)

(XLIX)

Where, \( R \) = various 4-chloro anilino cyanurated coupling components.
Ahmad et al. [114] have synthesized vinyl sulphone based fibre-reactive azo dyes (L) and applied on cotton fabric.

\[
\begin{align*}
\text{HO}_2\text{SO}_2\text{CH}_3\text{CO}_2\text{S} & \quad \text{N} = \text{N} \quad \text{R} \quad \text{N} = \text{N} \\
\text{N} = \text{N} \quad \text{SO}_2\text{H} & \quad \text{HN} \quad \text{NH} \\
\text{HN} \quad \text{NH} & \quad \text{SO}_2\text{H} \\
\text{N} = \text{N} \quad \text{R} \quad \text{N} = \text{N} & \quad \text{SO}_2\text{CH}_3\text{CH}_2\text{OSO}_2\text{H}
\end{align*}
\]

(L)

Where, \( R = \text{H-Acid, J-acid and Gamaa acid.} \)

Ali et al. [115] have synthesized disazo and polyazo ureido reactive dyes (LI) and applied on cotton fabric by the exhaust dyeing method. Different factors affecting the dye ability and fastness properties of such dyes are also investigated.

\[
\begin{align*}
\text{R} \quad \text{N} = \text{N} & \quad \text{NH} \quad \text{C} - \text{NH} \quad \text{NH} \quad \text{N} = \text{N} \quad \text{R}
\end{align*}
\]

(LI)

Where, \( R = \text{various cyanurated coupling components.} \)

Rizk et al. [116] have synthesized some new azo reactive dyes (LII, LIII and LIV). These dyes were applied to cotton fibre and their colour fastness to light, washing, perspiration and rubbing were also measured.

\[
\begin{align*}
\text{Cl} & \quad \text{N} \quad \text{Cl} \quad \text{H} \quad \text{N} \\
\text{Cl} & \quad \text{N} \quad \text{Cl} \quad \text{H} \quad \text{N} \\
\text{Cl} & \quad \text{N} \quad \text{Cl} \quad \text{H} \quad \text{N} \\
\text{Na}_2\text{SO}_3 & \quad \text{N} \quad \text{N} \quad \text{Na}_2\text{SO}_3
\end{align*}
\]

(LII)

Where \( R = \text{H, Cl, CH}_3 \)
Where, a: \( R=H, R_1=4-\text{SO}_3\text{H} \). b: \( R=\text{Cl}, R_1=4-\text{SO}_3\text{H} \). c: \( R=\text{CH}_3, R_1=4-\text{SO}_3\text{H} \).

d: \( R=H, R_1=2-\text{COOH} \). e: \( R=\text{Cl}, R_1=2-\text{COOH} \). f: \( R=\text{CH}_3, R_1=2-\text{COOH} \).

Lykidou et al. [117] have synthesized azo reactive dyes (LV) have been synthesized by coupling 1-amino-phenyl-4-beta hydroxyethyl sulfone sulfate ester with 1-amino-8-hydroxynaphalene-3,6-disousphonic acid (H-acid) and applied to cotton by exhaustion and digital ink-jet printing. Coloristic values of the dyed/ printed samples were as expected, that is, K/S values of the dyed samples were much higher than those of the printed ones, K/S values of the samples dyed with the ultrafiltrated dyes were higher than those with the initial dyes and the rest of the coloristic coordinates \( L^*, a^*, b^*, C^*, H \), were in line with strength changes of the dyes before and after ultrafiltration.

Where, \( X=\text{Na, K, Li} \).

**LITERATURE REVIEW QUINOXLALINE DERIVATIVES:**

**Quinazolinones**

Quinazolinones [118] are live nitrogen containing heterocyclic compounds. In 1869, Griess [119] prepared the first quinazoline derivative, 2-cyano-3, 4-dihydro-4-oxoquinazolinone, by reaction of cyanogens with anthranilic acid. Griess externally recognized the bicyclic nature of the product, which he called bicyano amido benzene and used until 1885 when the structure was known with some certainty [120]. Weddige [121] carried out systematic quinazoline synthesis following the observation that the formyl and acetyl derivatives of anthranilamide lost water on heating. He correctly interpreted this as a cyclization reaction and was first to realize the
possibility of tautomerism in the oxoquinazolines. The preparation of parent
quinazoline comes many years later when Bischler and Lang [122] obtained it by
decarboxylation of the 2-carboxy derivatives. A more satisfactory synthesis of
quinazoline was subsequently devised by Gabriel [123] who studied its properties and
those of its derivatives in greater detail.

**Numbering System of Quinazolinone**

The nomenclature of the quinazolinone ring system is as follows.

Quinazolinone is also known as phenmiazine, benzylene-amidine, 1,3-
diazanaphthalene or benzo-1,3-diazine or 5,6-benzo-pyrimidine. The term
phenmiazine was used by Wildman [124]. The numbering shown in the structure was
suggested by Paal and Busch [125] and is one in the remarkable use [126]. The
quinazoline having a hydroxyl group in 2- or 4- position forms a distinct class and are
tautomeric [127] with the corresponding keto dihydroxy quinazoline. Multifarious
data [128,129] indicates that 4-hydroxyquinazoline exists as an equilibrium mixture of
(a) and (b) in which the form (a) is the most favoured.

The 4-hydroxyquinazolilne tautomer with 4-keto-3, 4-dihydro-quinazoline, is
commonly named as 4(3H)-quinazoline is also the familiar name used for the system.
Today, the name 4-quinazoline has been universally accepted for 4-keto-3,4-
dihydroquinazoline.

**Synthesis of Quinazolinone**

The majority of synthetic route of 4-quinazolinone essentially proceeds from
anthranilic acid or its derivatives. A number of methods may be classified into
different categories according to the type of the components undergoing condensation.
TYPE – 1
This type includes condensation of
(1) N-acetyl anthranilic acid with aromatic amine in presence of phosphorus trichloride [130-132].
(2) N-acetyl anthranilic acid with acetic anhydride affording 2-methyl-3,1,4-benzoxazone that is subsequently allowed to react with an amine [133-138].
(3) N-acetyl anthranilic acid with an amine in a sealed tube [139].
(4) N-acetyl anthranilic acid with formamide [140].

TYPE – 2
This type includes condensation of
(1) Anthranilic acid with acid-amide [141,142].
(2) Anthranilic acid with cyanamide [143].
(3) Anthranilic acid with a compound containing –N=C-Cl system [144-146].

TYPE – 3
This type includes condensation of
(1) Acetanilide with urethane in presence of phosphorus pentoxide [147,148].
(2) Benzanilide imidochloride with urethane and subsequent cyclization [149,150].

TYPE – 4
This type includes condensation of
(1) Anthranilamide with acid chloride and subsequent cyclization of N-acylanthranilamide [151,152].
(2) Anthranilamide with acetic anhydride [153].

In addition to this, many other reactions are reported which lead to the synthesis of 4-quinazolinones [154-159].

Chromophoric potential of the 4(3H)-quinazolinone

The first commercial synthetic dye, Mauveine, discovered by Perkin in 1856 was also heterocyclic. Since that time the contribution of heterocyclic derivatives to colour chemistry has been considerable. The quinazoline nucleus is the key component of a number of colored products. The following literature shows the important role of the 4(3H)-quinazolinone ring as a chromophore.
P. S. Patel and co-worker [160] have synthesized heterocyclic monoazo dyes (LVI) from 4-oxoquinazoline. Dyeing properties of these dyes on wool and silk were assessed. Fastness properties have also been studied.

![Chemical Structure of LVI](image)

Where R= various coupling component.

Patel Divyesh and Patel Keshav [161] have also synthesized hot brand heterocyclic mono azo reactive dyes (LVII) by coupling of diazotized 2-phenyl-3-[4''-[((4''-aminophenyl) sulphonyl] phenyl]-quinazoline-4(3H)-one-6-sulphonic acid with various 2-chloro-4-nitro anilino cyanurated coupling components. Their dyeing performance on silk, wool, and cotton has been assessed.

![Chemical Structure of LVII](image)

Where, R= various 2-chloro-4-nitro anilino cyanurated coupling components.

Patel Divyesh R and Patel Keshav C. [162] have also synthesized reactive dyes (LVIII) based on 2-phenyl-3-[4''-(4''-aminophenylsulphonamido)] phenyl- (3H)-quinazolinionone-6-sulphonic acid. Their dyeing performance on silk, wool and cotton fibres has been assessed. The percentage dye bath exhaustion on different fibres has been found to be reasonably good and acceptable. The dyed fibres showed moderate to very good light fastness and good to excellent washing and rubbing fastness.
Where, \( R \) = various 4-chloroanilino cyanurated coupling components.

Patel Divyesh R. and Patel Keshav C. [163] have also synthesized some novel quinazolinone based monoazo reactive dyes (LIX) by coupling of diazotized 3-\{4-[4-amino-2-nitrobenzyl]-3-nitrophenyl\}-7-chloro-2-phenyl quinazolin-4(3H)-one with various p-chloro anilino cyanurated coupling components. These dyes gave good dyeing performance and fastness properties.

Where, \( R \) = various p-chloro anilino cyanurated coupling components

Patel Divyesh R., Bilimoriya Jignesh T. and Patel Keshav C. [164] have synthesised some new reactive dyes (LX) based on quinazoline. These dyes were synthesized by coupling of diazotized 3-[4-(4-aminobenzyl) phenyl] -2-[2-(4-fluorophenyl) vinyl]-quinazoline-4(3H)-one with various 4-chloro-2-nitro anilino cyanurated coupling components. Their dyeing performance as reactive dyes has been assessed on silk, wool and cotton fibres. The dyed fibre showed fair to very good light fastness and very good to excellent fastness to washing and rubbing. The dye bath exhaustion and fixation on different fibres were found to very good.

Where, \( R \) = various 4-chloro-2-nitro anilino cyanurated coupling components.
Patel Divyesh R. and Patel Keshav C. [165] have also synthesized heterocyclic monoazo reactive dyes (LXI) by coupling of diazotized 2-phenyl-3-[4’-[N-(4”-aminophenyl) carbamoyl]-phenyl]-quinazoline-4(3H)-one-6-sulphonic acid with various cyanurated coupling components. Their dyeing performance on silk, wool and cotton fibres has been assessed. These dyes were found to give a variety of colour shades with very good depth and levelness on the fibres. The percentage dye bath exhaustion on different fibres was good and acceptable. The fastness properties showed moderate to very good.

Where, $R$ = various 4-nitroanilino cyanurated coupling components.

Patel Divyesh R. and Patel Keshav C. [166] have also synthesized series of some new quinazolinone based MCT reactive dyes (LXII) by the coupling route of diazotized 3-[4-[4-amino-2, 6-difluorobenzyl]-3,5-difluoro- phenyl] -6-nitro- 2-phenylquinazolin-4(3H)-one (4) with a diverse range of o-chloro-p-nitro anilino cyanurated coupling components. All the newly synthesized dyes were tested for their in vitro antimicrobial screening against several bacteria and fungi. Some of the compounds showed significant antibacterial as well as antifungal activities.

Where, $R$= various o-chloro-p-nitro anilino cyanurated coupling components.
Parekh Nikhil M. and Mahera Kalpana C. [167] have synthesized heterocyclic monoazo reactive dyes (LXIII). Their dyeing performance on cotton, silk and wool has been assessed. Their colorimetric data (L*, a*, b*, c*, H* and K/S) have also been studied.

Where, \( R = H \)-acid, J-acid, N-methyl J-acid, N-phenyl J-acid, Chicago acid, Koch acid, Bronner acid, K-acid, Tobias acid, Sulpho Tobias acid, Peri acid and Metalinic acid.

Patel et al. [168] have synthesised monoazo reactive dyes (LXIV) based on 4,4'-methylene bis-(2-nitro aniline) and their dyeing performance on various fibres. These dyes gave good dyeing performance on wool, silk and cotton and showed very good fastness properties. These dyes were found to give a variety of colour shades with very good depth and levelness on the fibres.

Where, \( R = H \)-acid, Gamma acid, J-acid, N-methyl J-acid, N-phenyl J-acid, S-acid, Naphthionic acid, Peri acid, Bronner acid, Tobias acid, K-acid and Koch acid.

Patel et al. [169] have synthesised monoazo reactive dyes (LXV) and their dyeing performance on various fibres. These dyes gave pink, orange, brown and yellow shade on wool, silk and cotton having very good fastness properties. Exhaustion and fixation of these dyes are very good in order.
Where, $R = H$-acid, Gamma acid, J-acid, N-methyl J-acid, N-phenyl J-acid, S-acid, Naphthionic acid, Peri acid, Bronner acid, Tobias acid, K-acid and Koch acid.

Patel et al. [170] have also synthesised of monoazo reactive dyes (LXVI) based on 4-oxo-2-phenyl-4H-3,1-benzoxazine and their dyeing performance on various fibres. Their dyeing performance on silk, wool and cotton fibres has been assessed. These dyes were found to give a variety of colour shades with very good depth and levelness on the fibres. Exhaustion and fixation of these dyes are very good in order. The wash fastness and rubbing fastness of synthesis dyes are also good to excellent indicates the good penetration and affinity of these dyes to the fabric.

Where, $R = H$-acid, Gamma acid, J-acid, N-methyl J-acid, N-phenyl J-acid, S-acid, Naphthionic acid, Peri acid, Bronner acid, Tobias acid, K-acid and Koch acid.