General Introduction

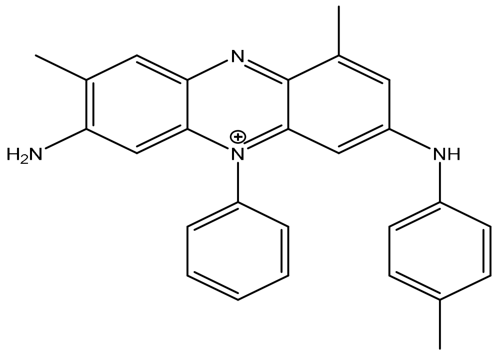
"Of all God's gifts to the sighted man, color is holiest, the most divine, the most solemn." – Ruskin

"Color is the place where our brain and the universe meet." – Klee

"Color! What a deep and mysterious language, the language of dreams." – Paul Gauguin

1.1 Introduction

Dyes are generally a coloured organic mixture or blend that perhaps apply for allowing colour to a substrate such as cloth, paper, plastic or leather. The middle of last century mostly the dyes were obtained from plants or animal sources. A dye is a compound that is employed for imparting colouring to objects. In the manufacturing of dye utilizing a chromogen-chromophore with auxochrome, chemical structure and coloration were correlated. For resonance and consequently coloration, a ring with an aromatic structure combined with a side chain is generally necessary. To make the final product, dyes are manufactured in the reactor, purified, and evaporated and mixed with the other components. Indigo, Tyrian Purple, Alizarin, Cochineal and Logwood were used as a Natural dye [1]. In overall, chemical compounds such as naphthalene interact either an acid or an alkaline substance, as well as an intermediate and a solvent, to generate a colour mixture. In 1771 Picric acid was obtained by Woulfe by reaction between indigo and nitric acid and use dyeing of silk. In 1856 William H. Perkin when preparation of quinine from aniline, accidently obtained black mass in reaction. He isolated a purple water-soluble compound that is called purple dye named Mauveine and he applied directly on wool and silk [2]. It gained popularity after Queen Victoria dressed a silk gown coloured with mauveine at the Imperial Exhibition of 1862 in the British capital.



Structure of Mauveine

The first azo synthetic dye called Bismarck Brown was developed in 1863 by Martius. After that Kekule (1858), Graebe and Liebermann (1868), Adolf von Bayer (1870), R.Bohn (1901), R.Clavel and H. Dreyfuss (1920) were developed different dye. In nineteenth century, most of dyes made from aromatic intermediate chemical derived from coal tar. Synthetic dyes are classified according to their application such as (1)Basic dyes

(2)Acid dyes (3)Mordant dyes (4)Direct dyes (5)Vat dyes (6)Azoic dyes (7)Disperse dyes (8)Sulphur dyes (9)Solvent dyes (10)Reactive dyes and according to their chemical constitution such as (1)Nitro and Nitroso dyes (2)Diphenyl Methane dyes (3)Triphenyl Methane dyes (4)Phthalein dyes (5)Azo dyes (6)Indigo Dyes (7)Anthraquinone dyes (8) Heterocyclic dyes. During development of synthetic dyes in 1954 first reactive dyes was synthesized under named Procion by Imperial Chemical Industries Ltd (ICI). Today most popular dyes for textiles coloration industries is reactive dyes for dyeing of silk, cotton and wool. Now novel classes of chromophores and reactive systems developed.

1.2 Introduction of reactive dyes:

Day by day, the textiles dyes industry jump up highest and highest. Dyeing of cotton with Direct dyes have poor washing fastness due to poor and weak polar and dispersion force between dye and cellulosic polymer chains. Furthermore, although research related the production of reactive dyes for several polyester and polypropylene fibers has reached the level of technical feasibility, such dyes are not yet commercially viable. The disruptive effect of reactive dyes on the synthetic dyestuff scenario has proven so noticeable that reactive dyes are currently the most significant category of dyes when it comes of both financial and bulk values. Reactive dyes are exclusive, contained covalent bonded with subtract. Rys and Zollinger defined a reactive dye as follows

"It is a coloured compound which has a suitable group capable of forming a covalent bond between a carbon atom of the dye ion or molecule and an oxygen, nitrogen or sulphur atoms of a hydroxy, an amido or a mercapto group respectively of a substract"

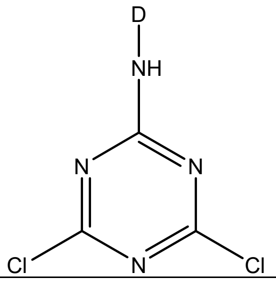
Reactive dyes are applied for cellulose by dyeing and printing method also used to polyamide fibres. Reactive dyes have high brilliancy in shade and have all high wet fastness properties. Reactive class of dyes are extremely important for cotton dyeing because they provide brilliant, strong colour with exceptional fastness. High fastness characteristics of fabric are caused by reactive dyes' strong covalent bonds between the dye molecules and polymer chains.

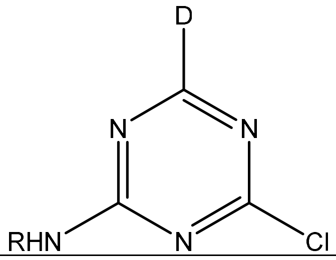
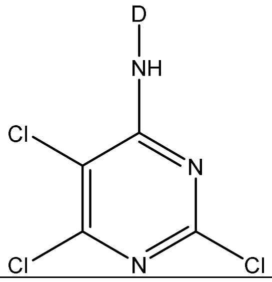
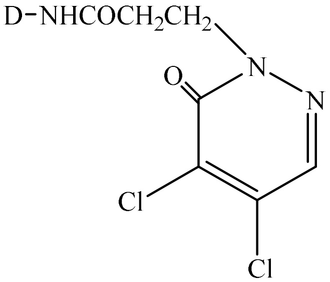
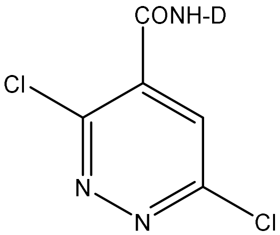
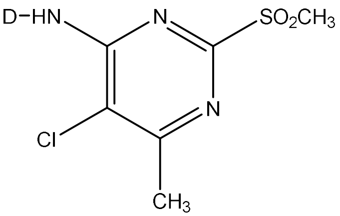
The first mercantile reactive dyes synthesized in 1956 by Rattee and Stephen named Procion M by ICI. These dyes were used for high brilliant shade for cellulosic fibres by continues dyeing method. Not only cellulosic fibres but reactive dyes were also used for Protein and polyamide fibres such as silk and wool. Recently express grow of reactive dyes because of the excellent feature like brilliant shades, very good wet fastness of fabrics and easy application. Procion Brilliant Red M-2B is the most popular example of procion dyes.

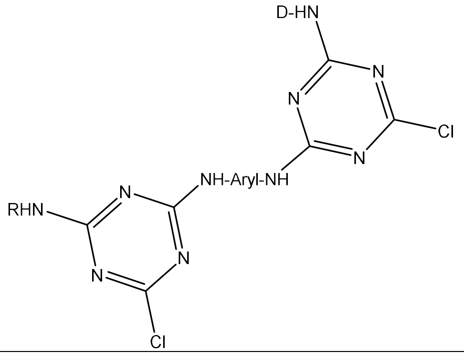
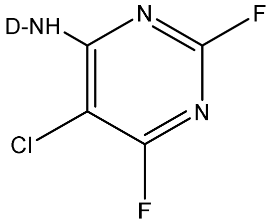
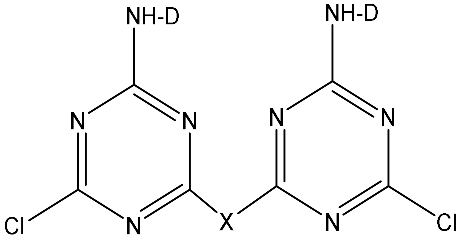
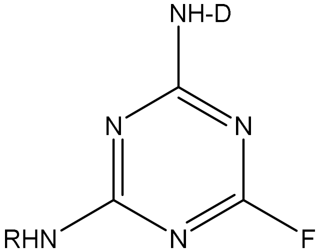
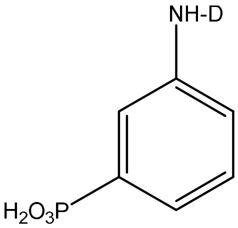
Procion reactive dyes is easy in application not also but have good brilliancy shade and tone also have good fastness properties.

1.2.1 Historical Evolution:

In 1949 Hoechst originally vinyl sulphone based reactive dyes first developed for wool fabric named as Remalan. According to Ratee and Stephen DCT (dichlorotriazine), a covalent link formed between a triazin's carbon atom and an oxygen atom in cellulose at higher pH levels[3]. In 1959 Ratee and Stephen joint awarded of Gold Medal from SDC(Society of dyes and colourist) for research of reactive dyes and their development. In 1960, ICI released Procion H-E, a range of reactive dyes based on MCT. After that top dye manufacturing company like BASF, CIBA, Geigy and Clariant was launched different reactive dyes with commercial named. Summary of development of reactive dyes is given in Table:1. Early in the 1980s, with Sumitomo's launch of Sumifix supra dyes, textile processors experienced a trend of incorporating different reactive groups into the same molecule. Levafix reactive dyes have excellent fastness properties and good exhaustion value. The research and development acceptation of the constant expand in the accessibility of subsisting goods from contemporary producers has been encouraged by reactive dyes. In the period of 1983-1988 around 270 commodity reactive dyes were joined to the textiles market. Due to excellent characteristics of reactive dyes the growing rate of annum is 3.9% world-wide. Manufacturers and dyers have requested more features, particularly outstanding dyeing fixation and all wet fastness characteristics, to increase the application of reactive commercial dyes. Currently several molecules are developed and improve fixation value of reactive dyes and excellent fastness properties achieve. Not only develop new reactive dyes but also modify application method which not effect environment.

Year	Brand Name	Supplier	Structure	Name
1956	Procion MX	ICI		DCT(Dichlorotriazine)

Year	**Brand Name**	**Supplier**	**Structure**	**Name**
1957	Procion H	ICI Ciba-Geigy		(Mono Chlorotriazine)
1957	Remazol	Hoechst	D-SO_2-CH_2-CH_2OSO_3H	VS (Sulphatoethyl Sulphone)
1960	Drimarene X	Sandoz		TCP(Trichloropyrimidine)
1964	Primazine P	BASF		Dichloro pyridazone
1964	Solidazol	Cassella		Dichloro pyridazone
1966	Levafix P	Bayer		MSP(Methysulphonyl pyrimidine)

Year	Brand Name	Supplier	Structure	Name
1967	Procion SP	ICI		MCT-Bis
1971	Levafix E-A	Bayer Sandoz		Diflorochloropyrimide(DFCP)
1972	Procion H-E	ICI		MCT-Bis
1978	Cibacron F	Ciba-Geigy		MFT(Monoflorotriazine)
1978	Procion-T	ICI		Arylphonic Acid

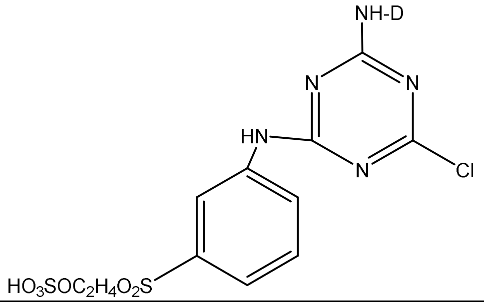
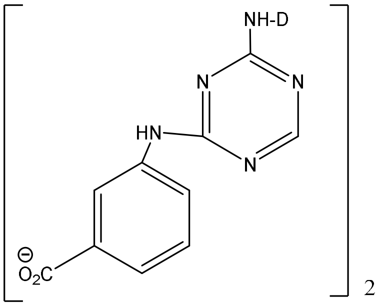
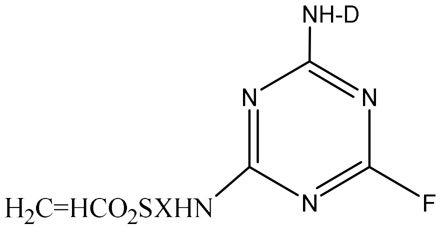
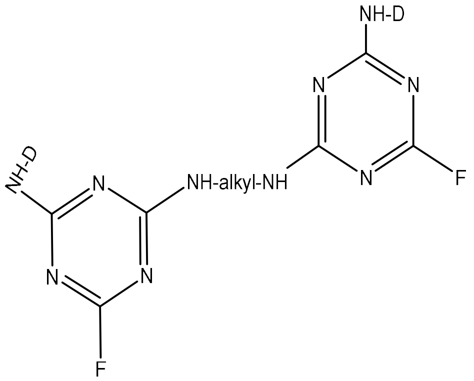
Year	**Brand Name**	**Supplier**	**Structure**	**Name**
1979	Sumifix Supra	Sumitomo		VS/MCT
1984	Kayacelon React	Nippon Kayaku		Bis-Nicotinotriazinyl
1988	Cibacron C	Ciba-Geigy		MFT/VS
1993	Cibacron LS	Ciba		Bis-MFT

Table:1 Development of Reactive dyes

1.3 Classification of Reactive dyes

The reactive synthetic dyes were mostly classified on the basses of commercial development. Reactive dyes classified in different group as follows:

(1) Cyanuric chloride nucleus base reactive dyes, which is sub classified in to (a) Mono-chloro triazine reactive dyes (hot brand) (b) Di-chloro triazine reactive dyes (cold brand)

(2) Chloro pyrimidine nucleus base reactive dyes

(3) Chloro pyridazine nucleus base reactive dyes

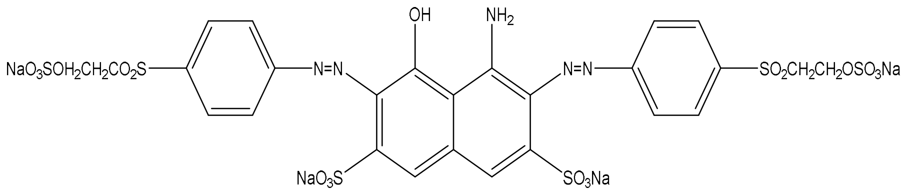
(4) Di-Chloro-Quinoxaline nucleus base reactive dyes

(5) Vinyl sulphone group base reactive dyes

(6) Acryl amide group base reactive dyes

(7) An epoxy groups.

The major popular group of reactive dyes is Vinyl sulphone based reactive dyes. The first dye was introduced by Hoeschst, now DyStar named Remazol and applied in alkali condition. After that in 1957 bifunctional reactive dyes was developed by DyStar named Remazol Black B (C.I.Reactive Black 5). After that Textiles dyes industries like Ciba, Sumitomo, Byer, Sandoz etc. developed different dyes by introducing different molecules in triazine ring [4]. The phenomenon of Reactive dyes has proceeded high speed. Reactive dyes for protein and polyamide fibres have also been manufactured. Although research for the manufacturing of some bi-functional reactive colours for polyester and polypropylene fibres had also achieved the stage of technical feasibility, such dyes are not yet commercially feasible[5,6]. Application of reactive dyes with less water is now most popular in dyeing unit so now several method are also develop.



CI Reactive Black 5

1.4 The Composition of Reactive Dye

Reactive dyes can be generated using the formula R-B-X Figure:1, where R is the chromogen. (Generating part of colour responsible for colour), X call reactive structure and B call bridging group such as -OCH_3,-NH_2, -$N(CH_2)_2$ etc.. W is water soluble group such as -SO_3Na and -COONa. Dyes molecules react with fibre F, X-F bond was developed called covalent bond[7]. Nature and stability of reactive dyes depends upon reactive group (X). Different colour of shade was obtained by changing (R) like Azo, anthraquinone and phthalocyanine derivatives. Mostly for the production of greenish yellow to Black shades azo compounds were used. Bright blue along with green tones with excellent light fastness properties of anthraquinone derivatives were used. For Turquoise shades nickel and copper phthalocyanine are used [8].

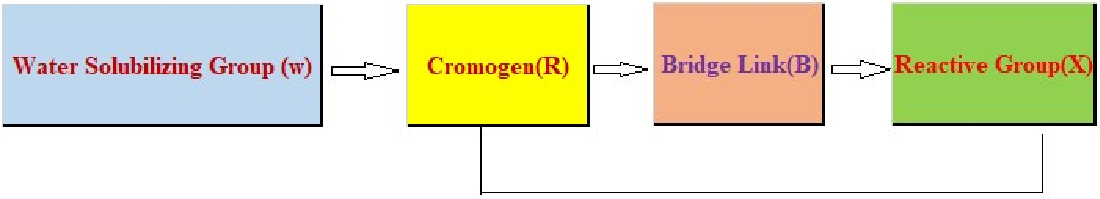


Figure:1 Fundamental structure of Reactive Colorant

In the theory, a leaving group (X) that can be nucleophilically displaced by the hydroxyl group of cellulose in the presence of an aqueous alkali should be enclosed by the reactive colourant.

$$(\text{Dye} - \text{X} + \text{Cell -O}^{-} \rightarrow \text{Dye- O} + \text{Cell} + \text{X}^{-})\ \text{Or}$$

An active -C=C- bond that can be added to the hydroxyl group from cellulose

$$(- \text{CH=CH}_2 + \text{Cell}- \text{OH} \rightarrow \text{-CH}_2- \text{CH}_2- \text{O}- \text{Cell})$$

The reactive dyes can be famed in to three group (i) Nucleophilic addition – elimination dyes (ii) Nucleophilic addition dyes and (iii) A phosphonic acid group fixation.

(i) Nucleophilic addition–elimination dyes:

When a leaving group in a reactive system is separated, polymer's chain is impacted by an interaction with a nucleophilic system. A common example of its action is the hot brand reactive dye along a -OH class of rayon or an -NH_2 group in keratin Figure:

2 and 3. The similar activity attribute for the competing hydrolysis reaction within water and the dye, when the dyestuff applied on fabric Figure:4.

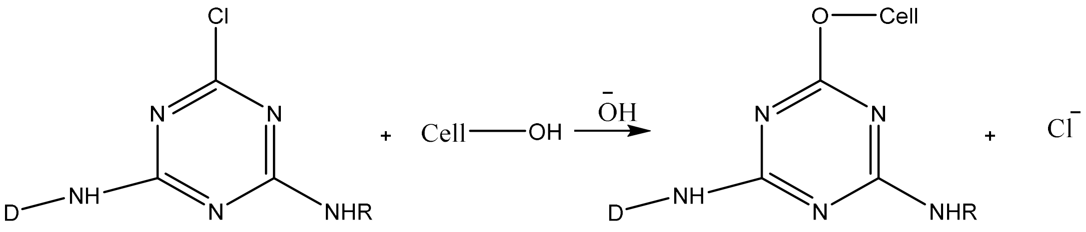


Figure:2 Cellulose and monocholotriazine dye reaction; D= Dye

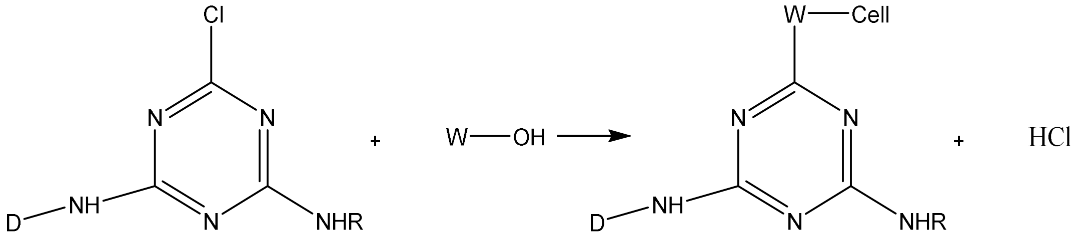


Figure: 3 Wool and monochloro triazine dye reaction; D= Dye

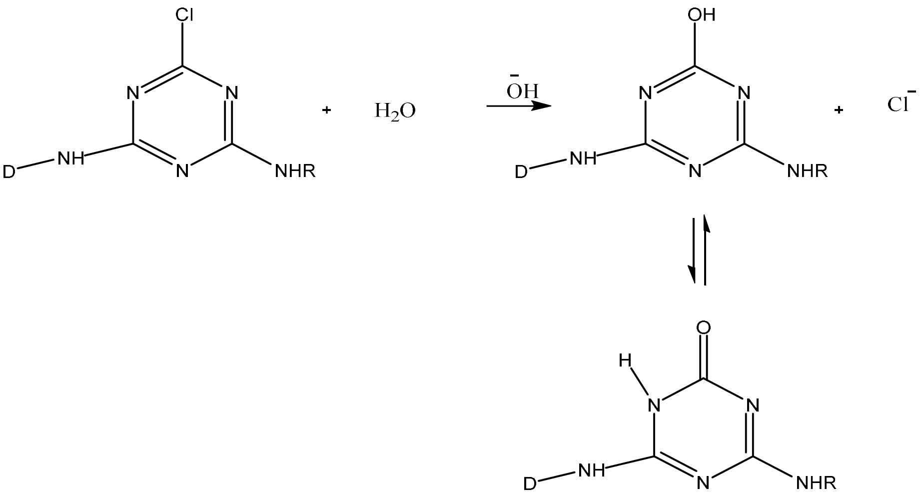


Figure:4 Monochloro triazine dye Hydrolysis; D= Dye.

(ii) Nucleophilic addition dyes:

The process by which a nucleophilic group from the fabric attaches past an activated carbon-carbon double bond in the reactive solution during the reaction between dye and fibre. Vinyl sulphone moiety is typically present in reactive structures. When it comes to the cost of the dyes used, the vinyl sulphone reactive system is typically not accessible. As an alternative and equally stable intermediate, sulphatoethylsulphone molecules are utilised. The fixing procedure, which has two stages is depicted in Figure: 5. Essentially similar dyes with β-sulphatoethylsulphamoyl group unquestionably create a cyclic combination capable of interacting with cellulose to allow a cellulose ether Figure: 6. Activated double bonds are further subjected to a competitive hydrolysis process in the method Figure:7. So, in reactive dyes there are two steps involve for fixation of dyes on fabric. First process is exhaustion and second steps is fixation. Some bi-function reactive dyes have low affinity with fabric and hydrolysis. Vinyl sulphone reactive system gives higher solubility of dyes resulted gives excellent wet fastness properties of dyes.

[1]

$$\mathrm{Dye\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OSO_3Na + NaOH}$$

$$\downarrow$$

$$\mathrm{Dye\text{-}SO_2\text{-}CH{=}CH_2 + Na_2SO_4 + H_2O}$$

[2]

$$\mathrm{Dye\text{-}SO_2\text{-}CH{=}CH_2 \quad + \quad Cell\text{-}OH}$$

$$\downarrow$$

$$\mathrm{Dye\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}Cell}$$

Figure:5 Fixation Process by Nucleophilic addition

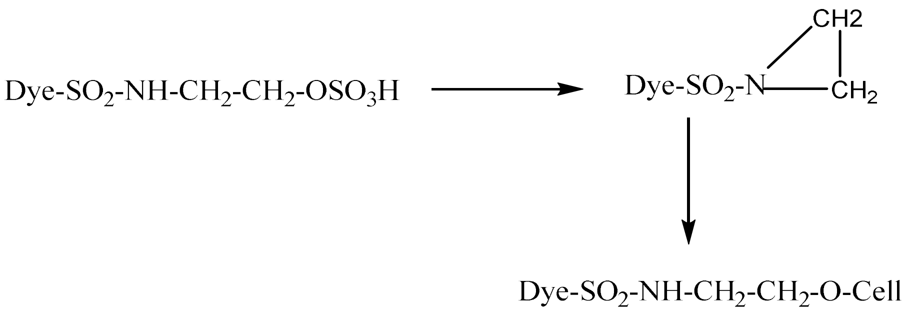


Figure:6 β-sulphatoethylsuphamoyl dye Nucleophilic addition

$$\text{Dye-SO}_2\text{-CH=CH}_2 + H_2O \xrightarrow{OH^-} \text{Dye-SO}_2\text{-CH}_2\text{CH}_2\text{-OH}$$

Figure:7 Reaction between water and vinylsulphone reactive dyes

(iii) A phosphonic acid group fixation

When cyanamide or a carbamide is present and the environment is acidic, a phosphonic acid reactive dyestuff can be fixed to cellulose at a temperature of about 200 °C. Figure:8 depicts the esterification method used in the reaction process. At that circumstance, an aggressive there is no reaction. The highest depth of dyes it could be obtained with utilising cyanamide maintain temperature 160 °C, despite unfavourable aggressive side effect of carbodiimide, which results in a disappointing degree of fixation.

Bifunctional reactive dyes have high percentage of fixation value. Compare to monofunctional reactive dyes selected bi-functional reactive dyes have excellent fixation value. In cold pad batch method maximum 75% fixation achieved, while 25% of dye is hydrolyzed. In bi-functional reactive dyes one group react as a 75% fixation same as mono functional reactive dyestuff, with 25% unreacted. 25% partially hydrolyzed but with help of second reactive group can react further. So that average 94% of the dyes applied on the fibers while only 6% dye is hydrolyzed or wasted in water. Bi-functional reactive dyes is perform better fixation in cold pad batch method compare to exhaust method. Mostly all bi-function reactive dyes are applied on cotton fabric with cold pad batch method. This method is not only giving high fixation values of dyes but more environmentally sound because less water was used. Most of textile's industries are used exhaust method of dyes but getting high depth of shade mostly cold pad batch method is used. In recent year now to reduce time microwave method is use. Now fluorine based reactive dyes most popular class of dyes, this dye gives good light fastness and require low salt for fixation DyStar introduced this class of dyes named with Levafix dyes. In these dyes presents of highly electrophilic fluorine group dyes have ecology parameter were control. So Levafix dyes have excellent fastness properties and fixation value.

1.5 Different Reactive system.

In General, Reactive dyes can be classified as bellow reactive system.

(i) Aliphatic (ii) Aromatic(iii)Heterocyclic.

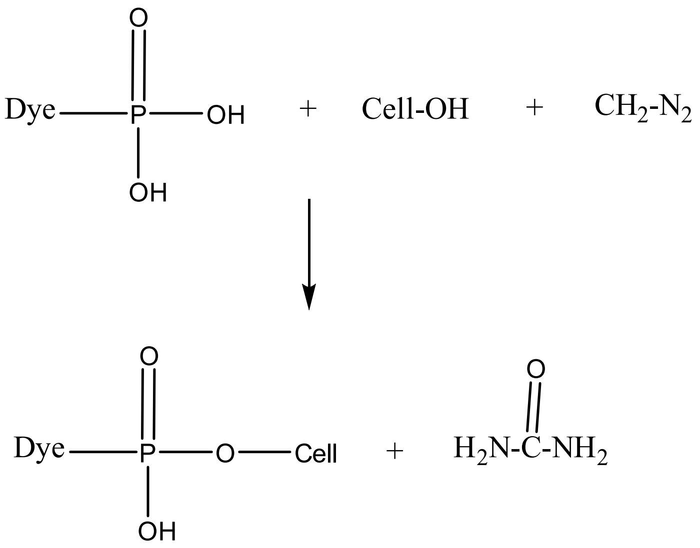
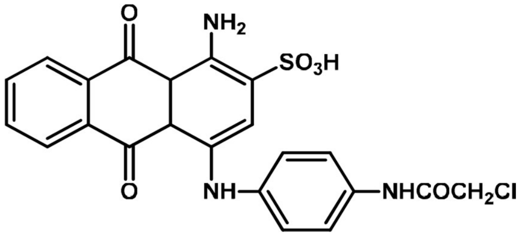


Figure:8 Phosphonic acid reactive dyes with cellulose

(i) Aliphatic Reactive System:

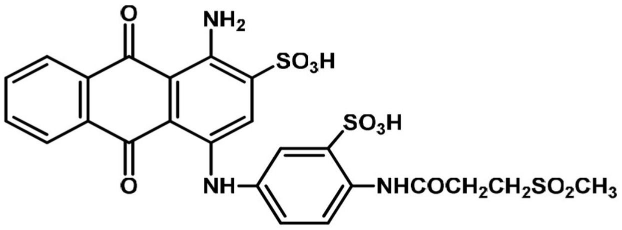
(a)Substituted Alkane -Mono Carboxylic Acid Amides:

In 1957 BASF introduced Dyestuff for the dyeing of Textiles Cellulosic containing choloroacetylamino group(I). The Fixation value of these Dyestuff are not high on cellulosic fibres. This type of dyes gives excellent light fastness as well shades and tone were very brilliant. Choloroacetylamino group presents in dyes molecules have good brilliancy in shade but not high affinity to cellulosic material. BASF also modified the Choloroacetylamino group of dyes for getting good wash fastness. In this time BASF also produced high light fastness dyes which have contain choloroacetylamino group. This type of dyes has good light fastness properties but washing fastness is very poor compare to other dyes, so this class of dyes was not most popular.



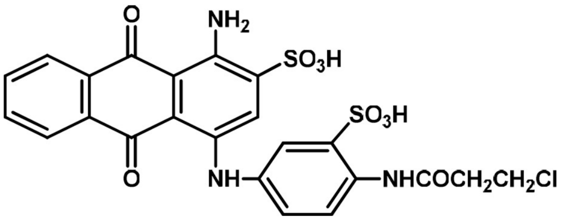
(I)

BASF developed a patent for colours containing Sulphonylpropionamide (II) anthraquinone azo and phthalocyanine dyestuff are examples of sulphonyl group and are characterised and recorded.



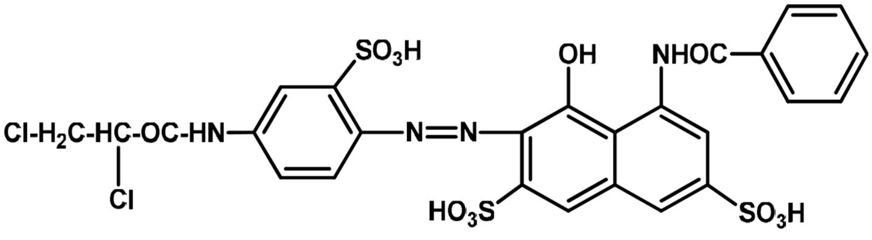
(II)

CIBA developed water soluble dyes for dyeing of wool fabric dyestuff containing β-chloro propionylamino group (III) this dyestuff has less affinity for printing and continues dyeing for cellulosic fibre.



(III)

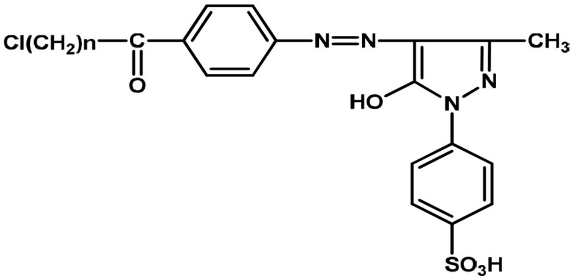
In a CIBA patent [9] relating to α, β-dihalopropionamides (IV) reactive dyes for cellulosic fabric were developed. Innovative dyestuffs are produced using dichloro- or dibromo propionic acid in a variety of techniques. Amidations and alternative isobutyric acid amides and substituted aliphatic carboxylic acid were competing as a new reactive component[10].



(IV)

(b)Substituted Aliphatic Ketones:

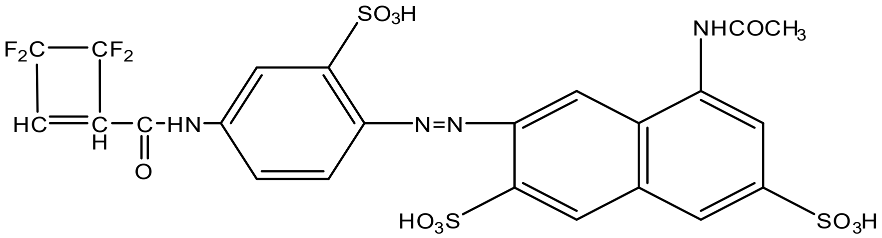
BASF established the dyestuff for colouring cellulose in the presence of alkaline solutions that contain chloromethyl- or chloroethyl aryl ketone(V), these synthesized dyes are suitable for continues and printing method [11].



n = 1,2 (V)

(C) Substituted Cycloalkane Carboxamide:

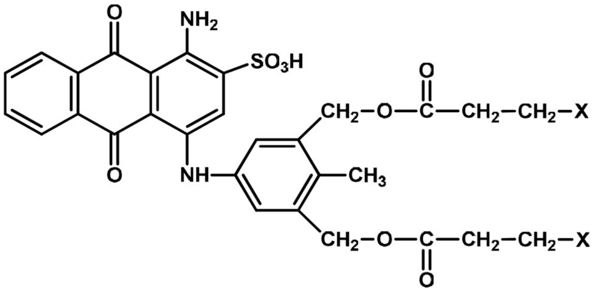
Tetrafluoro cyclobutene carboxamides is productive reactive dyestuff group (VI) developed by Farbwerke Hoechst Company [12]. Several patents claimed under Fluoro Cyclobutene Carboxamides by Hoechst.



(VI)

(d) Substituted Alkane-Monocarboxylates:

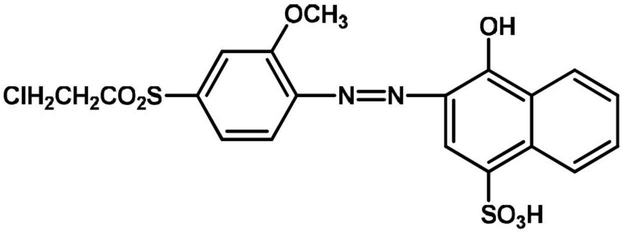
General Aniline and Film corporation limited company (GAF) was developed new reactive dyestuff group (VII), have good yield and excellent wash fastness properties. Dyes were suitable for cellulosic material and wool fabric also.



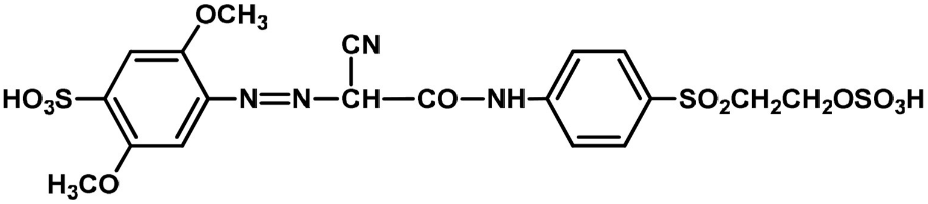
(VII)

(e) β-Substituted Ethyl Sulphone – Vinyl Sulphones:

Farbwerke, Hoechst and Sumitomo made large number of patents with used vinyl sulphone (VIII and IX), Generally β Subsistence X = -Cl, -N (Alkyl)$_2$, -SO_3H, -OPH_2O_3 and preliminary -OSO_3H are used. CIBA developed reactive dyes containing β-halo ethyl sulphone group [13]. Mostly easily eliminated β-substituted e.g., X= -Cl are used for new development of reactive dyes. Vinyl sulphone group is often easily substituted with the aryl nucleus of the azo element or coupling components for the production of synthetic azo reactive colourants, although bridges are enclosed e.g.-NH-, -$(CH_2)_n$, -$CONR(CH_2)_n$-, -SO_2NRAryl-, -CONRAryl- and -$NRSO_2$Aryl- along with aryl nucleus and the vinyl sulphone group. This class of dyes are most popular class of dyes.



(VIII)



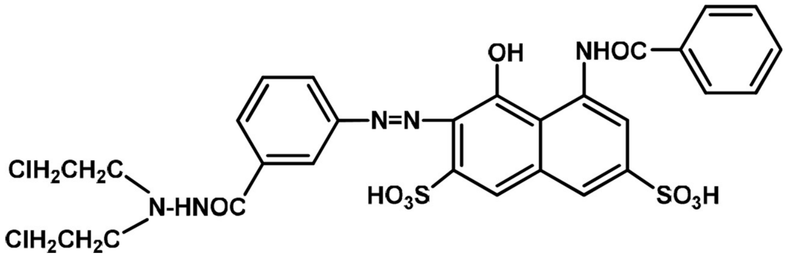
(IX)

(f)Alkene Monocarboxamide:

Colorants that react with the acrylamide-containing members of the β-chloropropionylamide class do so in a rather slow manner. Alkene monocarboxamide based dyes are limited applicable for the exhaust of cellulosic fabrics. Class of Reactive series dyes in this category are appropriate for printing and cold pad batch applications. Less stronger dyes belong to the crotonamide class.

(g) β-Substituted Ethylamine Derivatives:

So many dyes were developed by BASF company. Ethylamine derivatives base reactive dyes were synthesized. The dyes have good compatibility with cotton fabric and dyes have excellent fastness properties. During the application of dyes in alkaline conditions bond was formed.

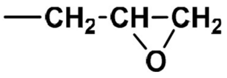


(X)

In 1956 BASF developed colorant have β-haloethylamine group for textiles cellulosic material [14]. All ethylamine derivatives' group was attached on β position, which create a bond under alkaline condition. Sandoz claimed novel dyestuff containing N, N-bis-(β-chloroethyl)hydrazide(X).

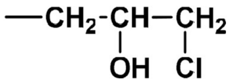
(h) Epoxide Derivatives and Their Precursors:

Water soluble reactive dyes which have containing (a) and (b) gives high wet-fastness properties.



$-CH_2\text{-}\underbrace{CH-CH_2}_{O}$

(a)

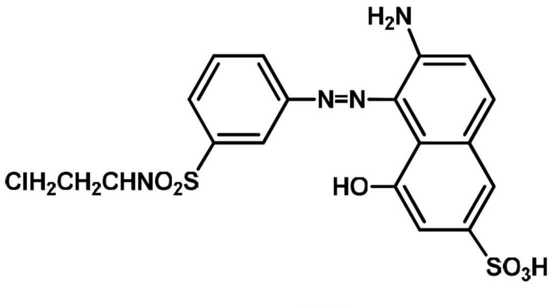


$-CH_2\text{-}\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

(b)

(i) β-Substituted Ethylamine of Sulphonic Acid:

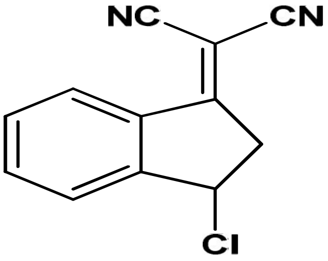
ICI described the water-soluble reactive dyes having the N- β-halo ethyl sulphonamide (XI) group [15]. This class of dyes have brilliancy in shade as well as good fastness properties. Dyestuff fixed on material with alkali medium.



(XI)

(B) Carrier Systems for Aromatics:

As of groups -C≡N- and $-NO_2$ both activate halogen groups in the ortho or para positions in aromatic rings [16]. This class of dyestuff are not used in textiles industry. Aromatic systems of this class of dyes are described below (XII).



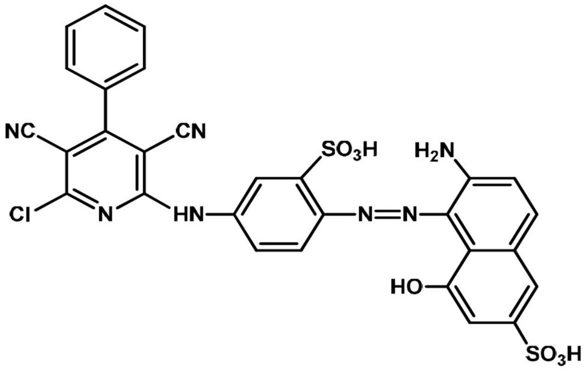
(XII)

[C] Heterocycle Carrier Systems:

In this class several derivatives have been developed and described as below.

(a) Pyridine derivatives:

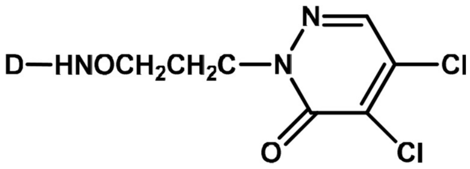
Reactive dyes that are easily fixed and produced by the condensation of amino dyes with 3,5-activated 2,6-dichloro pyridine derivatives (XIII). In normal dyeing and printing condition, not take easily formation of covalent bond with cellulosic system in pyridine or quinoline systems which have halogen substituents attached [17].



(XIII)

(b) Pyridazone derivatives:

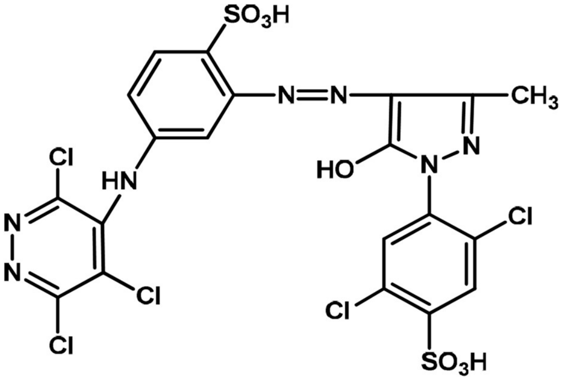
Technical significance in reaction for this class of reactive dyes, the position 4 reaction of 4,5- dihalo derivatives results in vinylogous carbonyl halides. The nitrogen atom in this reactive complex is not an aromatic hydrogen heterocyclic molecule.



Drimarine

(c) Pyridazine Derivatives:

Printing and batch cold pad dyeing are more appropriate for reactive dyes with chloropyridazine groups. The following (XIV) dyestuff obtained from condensation of tetrachloropyridazine with 1,3 diamino benzene-4-sulphonic acid in an aqueous alcoholic medium [18].



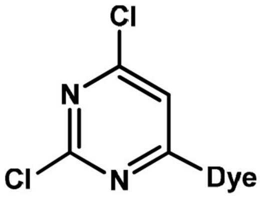
(XIV)

(d) Pyrimidine Derivatives:

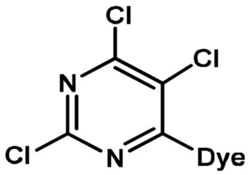
The most widely used heterocyclic system is pyridine.

Chloropyrimidine nucleus containing Reactive Dyes:

(a) Dichloropyrimidine Type:



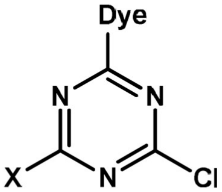
(b) Trichloropyrimidine Type:



Reactive Colorant Containing Cyanuric Chloride Nucleus:

Reactive dyes in this family include cyanuric chloride, which has three labile chlorine atoms that can be substituted out for amine salts or hydroxyl compounds in succession. Below is a description of reactive dyes made from cyanuric chloride:

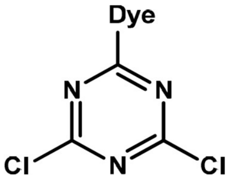
(a) Procion H (Cibacron)



Monochlolorotriazine dyes reactive colorant

X= The chlorine or heterocyclic residue is bonded to a free amino group in an aromatic or aliphatic amine or colour.

(b) Procion M

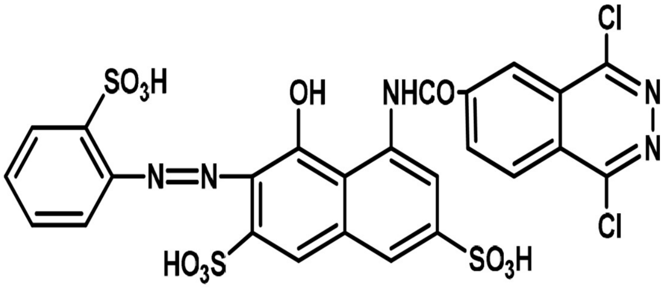


Dichlorotriazine reactive colorant

1,2,4-triazine derivatives are widely used as a reactive component. 3,5-dichloro and 1,2,4-triazine in aqueous solution was condense with amino azo dyestuff at 0-5ºC in pH 5-6 forming a reactive dyestuff.

[D] Phthalazine derivatives:

This class of reactive dyes developed by Byer and dyes suitable for printing and continuous dyeing process. They introduced dyes with trade named Elisiane, dyestuff containing 1-4-dichlorophthalazine-6-carbonyl chloride [19].



Elisiane Brilliant Red B **(XV)**

1.6 Application of reactive dyes:

There are main four technique used for application of reactive colorant used in textiles industries; Exhaust dyeing , Pad-Batch dyeing process, Continues dyeing process, Printing method [20].

1.6.1 Exhaust dyeing process:

The main idea behind exhaust dyeing is to use neutral or mildly acidic conditions to exhaust dye from the fibre. For preparation of dyebath first dye completely dissolved in water and urea used as solubilizing agent in some of dyes, common or glauber salt used as electrolyzing agent. Below these conditions, the reaction between dye and fabric is very slowly. The dye-fibre fixation happens after the increase the pH value of dyebath with adding of alkali [21]. After the dyeing unfixed dyes, alkali and electrolyte is removed with the wash off process. These exhaust methods are frequently prorated among four various group, there are three categories distinguished by the types of fixations and exhaustion, while a fourth category is an all-in technique.

1.6.1 (a) The Conventional Method:

In the traditional procedure, dye and electrolyte are added to the bath after it has reached fixation temperature and the bath is then further heated to fixation temperature before alkali is added. When rapid exhaustion is unwanted and if equipment of dyeing has adroitly heating command at that time the conventional method is used. The salt addition and heating rate of temperature are not well-ordered causes unlevelled dyeing.

1.6.1 (b) Dyeing method with constant temperature:

In constant temperature dyeing method, at beginning of rotation temperature remains continues concluded al1 over the exhaust method. Dyestuff is mixed at launch of rotation. Electrolyte further added at starting point and later alkali is joined following appropriate time interval to prevent fibre-dye fixation take place. The operation of this technique is simple and widely used. The problem of maintaining an inconsistent temperature during heating is completely removed.

1.6.1(c) Dyeing method with high temperature:

In this process, the dyeing process is started at a raised heating, and then the temperature is reduced before alkali is added to fix the color. At beginning a higher temperature promotes higher levels of high-speed diffusion, improved migration and dye levelling. Also, for dyes with high substantivity, fixing is significantly lower. The idea behind this method is to dye garments while simultaneously using high twist yarns, woven fabrics, or rayon viscose materials[22,23].

1.6.1(d) All-In method:

Alkali colour and salt are added during this procedure at the beginning of the rotating dye solution bath. To decrease the hydrolysis of reactive dyes alkali added at the beginning at low temperature. The simplicity operation and less time cycle is the main advantage of this method, afterward dye and alkali are added at starting point of process. This method is not suitable for less penetrate goods. Controlling the heating rate of temperature is necessary for levelness of dyeing as well as exhaustion, fixation and colour yield [24]. In dyeing of small process house where dyed with light and pale colour, this method is mostly used. Less water is used in this method.

1.6.2 Pad Batch semicontinuous dyeing process:

The low liquor rations and object temperature is necessary for conduct this method. The main purpose of this method is to apply a dye and alkali liquids to the products after that as uniformly to the batch as possible. After pass the goods from a liquor the goods are then enveloped with after being removed from the liquor, the products are next wrapped in polyethylene to prevent water from dissolving and the chemical reaction of carbon dioxide in the air with alkali. The material goods beams are kept in a room with minimal lighting and no heat. Batching time depends upon the reactivity of dyes, it can be 2 to 4 hours or 16 to 24 hours. After that the goods were washed with cold and hot water. Pad Batch dyeing process is more popular in textiles industries due to low cost, less water consumption, reduced use of energy and auxiliary resources also resulted in lower labour expenses and water effluent production[25]. About 5000 meters lot size is dyeing considered in this method that is economical lot size compare to other methods [26].

1.6.3 Continuous process of dyeing:

This method provide advantages during long run are mandatory in a bounded range of shades. Very good repeatability is achievable with economizing in keeping and Employment expense[27]. The main technique involves saturated the cloth material with dye liquor in an open width using a padding part. Both a single-bath method and a double-bath method could be used to complete this phase alkali is combined in a single pad bath during the process of one bath, but during the process of two baths, the hydroxide is coated in the subsequent bath. After that a saturated material are conquered to the fixation method with using dry heat, washing off is done before thermos fixation or wet heat such as steam fixation[28,29]. There are four unique categories that make up the continuous dyeing process.

1.6.3.1. Pad-Dry-Pad-Steam (The Conventional Dyeing Method):

With this procedure of dyeing, the first padder is used to apply the dye and after that the fabric is dried, in order to produce even coloured fabrics, many dyes smoothly undertake migration while drying. Perhaps required in the first pad bath are salt and antimigration. The material is removed from drying by passing through a second pad wash containing alkali and salt and bleeding towards the pad bath should be as little as possible. After that materials are steamed and washed off. If a thermosol step is placed in between the drying and the second pad processes, the traditional dyeing procedure is advised for dyeing polyester/cotton blends [30].

1.6.3.2 Pad steam dyeing method:

In this procedure, the pad bath is also subjected to the dye, alkali and salt. Dye hydrolysis shouldn't be an issue if dye and alkali are regularly added to the pad from several feed tanks. Although, the concentration of salt may cause problems of dye solubility[31]. This technique was created to allow for the elimination of the middle, expensive drying stage. For fabrics with migration problems during the intermediate drying process, this procedure is primarily used. This method is utilised for dyeing cloth for towel[32]. This type of method the concentration of salt is most important because after pad fabric direct steam so chance of un even dyeing. Salt and dye solution continue pass for getting good dyeing result.

1.6.3.3 Wet on Wet method:

In this process to achieve dye fixation before steaming fabric is padded with solution of dye after that fabric is passed from salt and alkali. At high concentration of alkali causes lead to bleeding of dye in wet-on-wet sequence method[33]. Towels and pile textiles are the main materials utilised for this technique. Wet to Wet sequence approach is primarily used for deep shade varieties.

1.6.3.4. Pad-Dry-Cure method:

With use of sodium bicarbonate and urea some reactive dyes are padded. Fixation of dyes is caused by the urea that gives the fibre humidity[34]. However, the use of urea, which results in the creation of fumes during curing, has been a limitation of the pad-dry-cure technique[35]. The E-control method is a joint project between BASF and Monforts that is currently making some progress in the continues reactive dye application. In this method dichlorotriazine reactive dyes applied with use of sodium bi-carbonate only, no other chemical like urea, salt, silicate are used. By setting the relative humidity content in the dryer at 25%, the E-control approach gets rid of the typical chemicals that are utilised. The method consists padded the fabric with dye and alkali, at 120 ^{0}C two minutes drying and then wash to remove unfix dyes[36]. Compare to other continues method E-control method gives higher colour yield. The biggest drawback of this approach is that it necessitates a comprehensive assessment of the dryer's humidity.

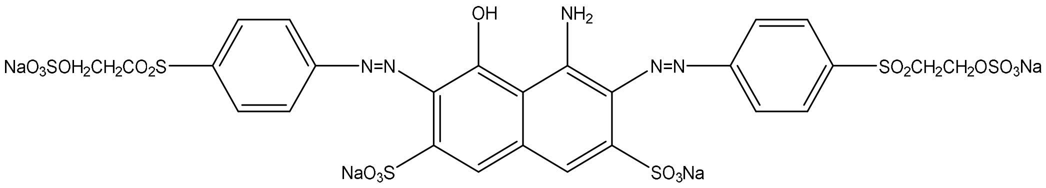
The infrared heating for dyeing of cotton fabric with reactive dyes used continues method now a day investigated. The dye fixation achieved with very short time in this method. The infrared heating continues method gives higher percentage yield of colour, this technique is beneficial for reducing the adverse ecological impacts of unfixable dyes and dye support in the dyestuff effluent[37].

1.6.4 Printing

For the application of reactive dyestuff textiles printing is a high popular area. There is no more fundamental difference between dyeing of reactive dyes and printing method. There is different direct printing method for application of reactive dyes with cellulosic fibers. Sodium carbonate or bicarbonate can be used to make the print paste, urea, sodium alginate and oxidising agents are examples of thickening agents, using this print paste, fabric can be printed, which can then be dried, steamed, washed, and dried. Reactive dyes are fixed on cellulosic fibres using saturated steam and dry heat fixation during atmospheric steaming. Excellent water solubility must be a characteristic of the reactive dyes. Yet, compared to voluntary dyes, the chosen dyes have lower substantivity against cellulose. The depth fixation of dye and colour yield depends upon the temperature and processing time of steaming. The washing out of hydrolyzed reactive dyes is easier in this method. The main disadvantage of this method is low fixation value only average 60% [38,39].

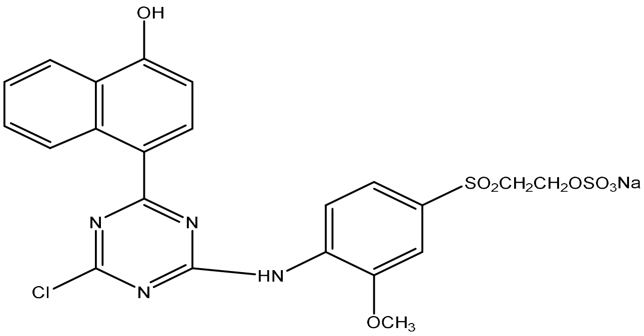
1.7 Literature review

The synthesis of bi-functional reactive dyes it is more important to selection of the reactive group and the chromophore. From last twenty-seven years that many scientists and researchers have been developed the new reactive dyes with modification in structure of dyes. Several reactive dyestuffs are available in textiles market, such reactive dyestuffs are known as bifunctional and hetero-bifunctional. The bifunctional reactive dyestuff have excellent fixation value and good fastness properties such as CI Reactive Black -5 containing two sulphatoethylsulphone precursor groups. On cotton fabric with cold pad batch method 90% fixation value achieved when apply on cotton fabric. Many research has been developed bi-functional reactive dyes with introduced new molecules in dyes structure to improved solubility and fastness properties.



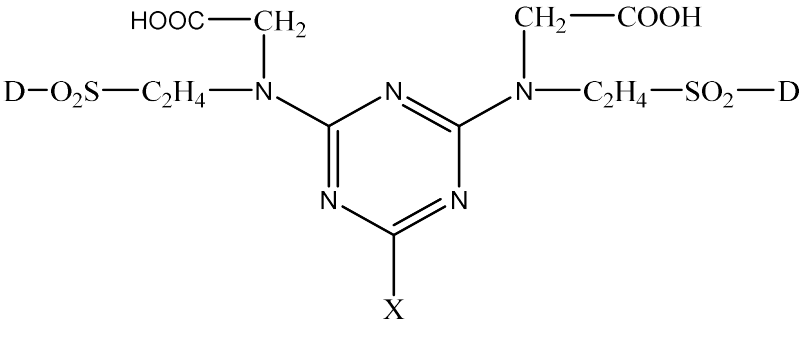
CI Reactive Black 5

M.M. Dalal et al., [40] have been prepared bifunctional reactive azo dyes derived from 2-chloro-4-[4′-(β-sulphatoethyl)-sulphonyl-2-methoxyanilino]-6-(4″-hydroxy-1″-naphthyl)-s-triazine. These synthesized reactive dyes have high degree of fixation. The fastness, exhaustion and fixation qualities of synthetic dyes are outstanding. All dyes have good solubility in water. Synthesized dyes have excellent light fastness and washing fastness properties. This type of dyes also used with different method of dyeing. The presents of vinyl sulphone systems in reactive dyes resulted good exhaustion quality of dyes. This bi-functional reactive dyes have when applied on cotton fabric high brilliancy of shade was achieved.



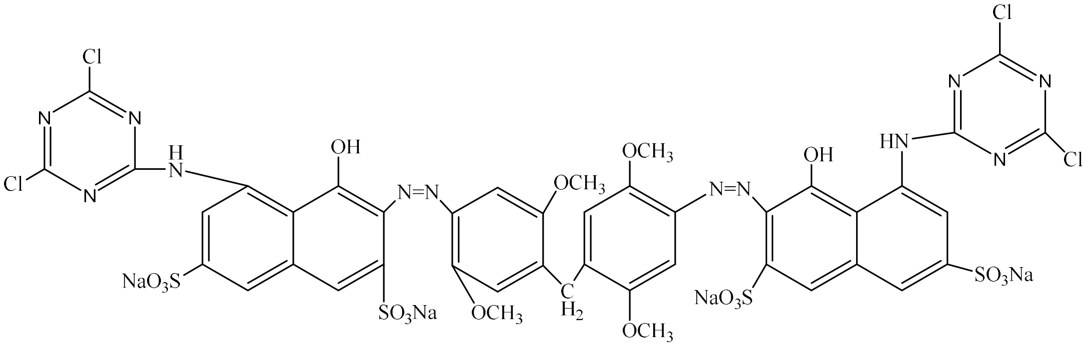
Bifunctional reactive dyes synthesized by M.M. Dalal et al

M Lewis et al., [41] have been synthesized by reacting vinyl sulphone dye and glycine and after that next condensing the N-CMA-ES dye with cyanuric chloride to prepare bis-NCMA-MCT-bis-ES dye, then additionally reacted with extra nicotinic acid to obtain a bis-N-CMA-MQT-bis-ES dyes. Cotton cloth was dyed using all synthetic dyes under various conditions, including pH and temperature. All bi-function dyes have good fixation value at several dyeing conditions.



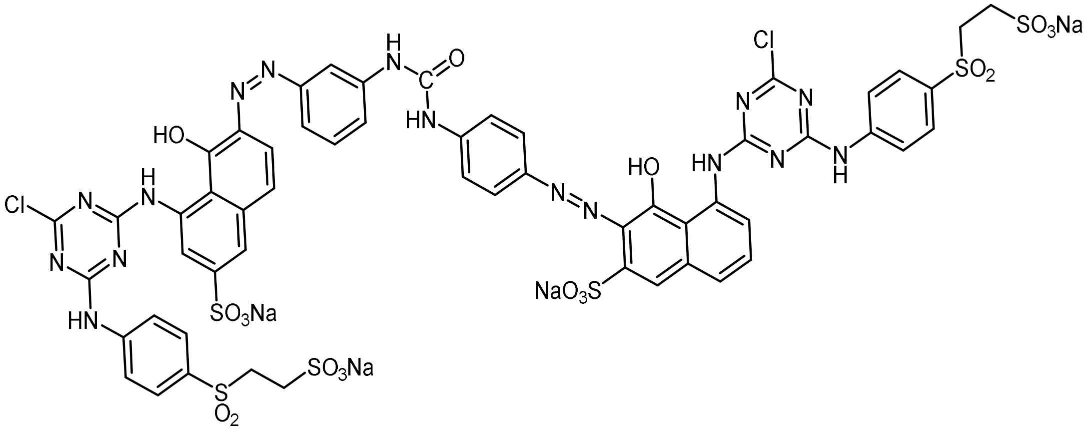
Reactive dyes synthesized by D M Lewis et al

Bhavesh M. Patel et al., [42] have been developed by cyanurating various coupling materials, such as H-acid, J-acid, N-methyl J-acid, and Gamma acid, with tetrazotized 4,4-methylene bis-2,5-dimethoxy aniline. Excellent colour consistency was achieved with all produced dyes on cotton, silk and wool fibres. Several coupling component gives different colour and fixation values. Dyes when applied on cotton fabric maximum fixation values are achieved.



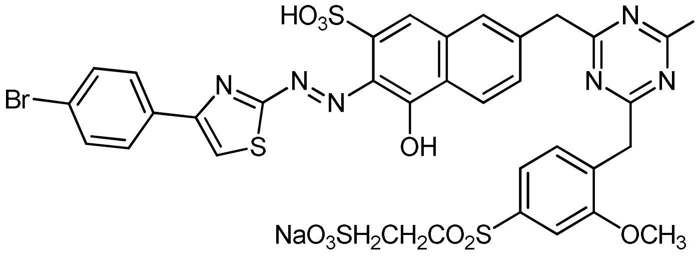
Reactive dyes prepared by Bhavesh M. Patel et al

N.F. Ali et al., [43] have been prepared bisazo and polyazo ureido reactive dyes and studied on cotton fabric. Intermediate ureido diamine was used for synthesized dyes. synthesized dyes have contained bis(monochlorotriazine), bis (monochlorotriazine / sulphatoethyl sulphone or the bis (sulphatoethysuphone) reactive system. The ureido reactive dyes have moderate to good fastness characteristics.



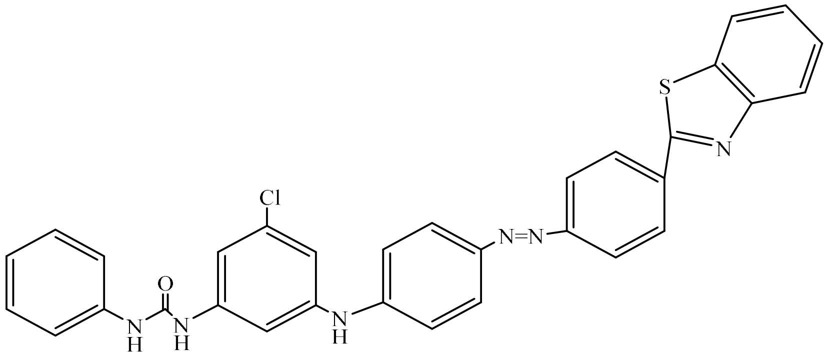
Ureido reactive dyes prepared by N.F. Ali et al

A.I. Ezeribe et al., [44] using 4-(4-phenyl)-1, 3-thiazol-2-amine and 4-(4-bromophenyl)-1, 3-thiazol-2-amine, bifunctional reactive dyes have been created. To create the reactive dyes, the diazo components of 4-(4-phenyl)-1, 3-thiazol-2-amine and 4-(4-bromophenyl)-1, 3-thiazol-2-amine were coupled with J-Acid and additional coupling components. Prepared dyes were examined on cotton fabric resulted good fixation value and excellent fastness properties. This bi-functional reactive dyes also used with different application method to achieved good fixation values like cold pad batch method.



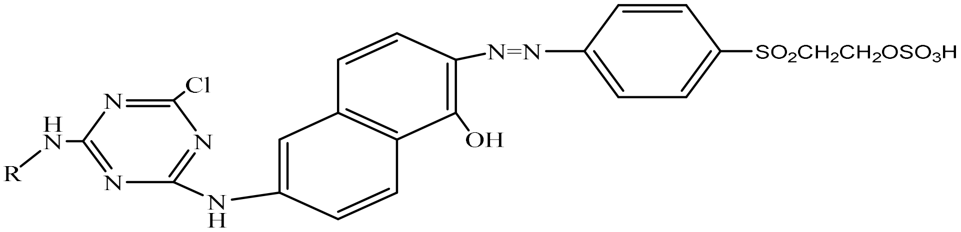
Reactive dyes prepared by A.I. Ezeribe et al

Snehal lokhnadwala et al., [45] prepared novel reactive dyes from benzothiazol derivative. Para amino benzoic acid, 2-amino thiophenol polyphosphoric acid, and the diazonium salt of the resulting amino compound were used to generate several benzothiazole derivatives, which were then coupled with various primary amines. Then reaction with cyanuric chloride and phenyl urea resulting novel reactive dyes. All synthetic dyes have good fixation and fastness characteristics and were applied to silk and wool fabrics.



Reactive dyes prepared by Snehal Lokhnadwala et al

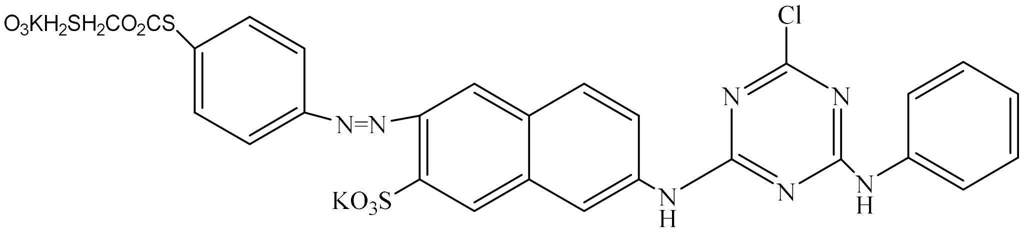
Xion Wei et al.,[46] reactive dyes have been created by adding benzene sulfonamide derivatives to the triazine ring. To prepare a novel series of hetero-bifunctional reactive dyes, cyanuric chloride was combined with benzene sulfonamide and its derivatives. When cyanuric chloride is condensed with benzene sulfonamide and J-acid is utilised as a coupling agent, 4-(β-sulfatoethysulfonyl) aniline is used as the diazo component. Synthesized dyes studied on cotton fabric, the dyeing results showed that the all dyes have good light fastness properties and excellent fixation value.



Reactive dyes prepared by Xion Wei et al

Where R is benzene sulfonamide derivatives

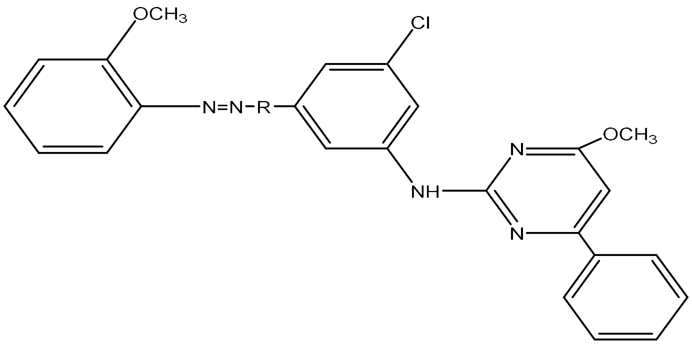
KM-type ethoxy containing reactive dyes prepared by Qiushui Zhang et al., [47]. KM-type ethoxy reactive dyes (14 reactive dyes) were synthesized with J-acid, H-acid and Gamma acid used as a coupling component, 1-aminobenzene-4-(2-sulphoethyl)-sulphone was diazotized then coupled with J-acid intermediates containing an anilino, 4-sulophenyl-1-anilino, ethylamino or ethoxy group to synthesized J-acid mono azo reactive dyes. KM-type ethoxy dyes have low hydrolysis resulted excellent depth of shade and good fixation value.



Reactive dyes prepared by Qiushui Zhang et al

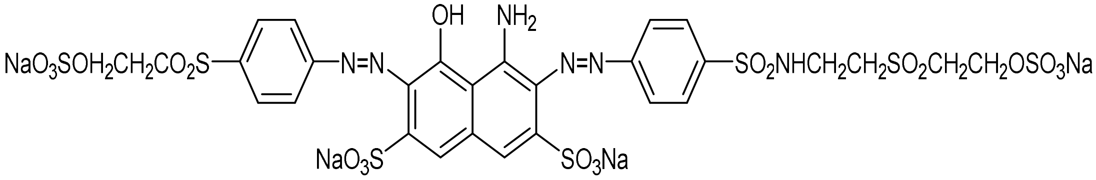
The maximum fixation was attained at 75 ºC when all synthetic reactive dyes were applied to cotton fabric at various pH and temperature levels. All dyes have excellent wet fastness properties.

Alkesh B. Patel et al [48] have organised using o-anisidine as a diazo component, 2-amino-4-(4-methoxyphenyl)-1-phenylprop-2-en-1-one serves as the foundation for monoazo reactive dyes. All synthetic dyes, which were used on cotton, wool and silk fibres have outstanding fastness properties. All mono azo reactive dyes dyed with cotton fabric at 80 ^{0}C excellent fastness properties achieved. Mono azo reactive dyes gives good fixation values on wool and silk fabric also due to presence of triazine ring in reactive dyes.



Azo reactive dyes prepared by Alkesh B. Patel et al

Lilli Yang et al., [49] have been prepared bi-functional reactive dyes containing benzsulfonamide moiety. Prepared dyes have azo and benzsulfonamide auxochromic groups. The novel dyes expose developed substantivity as well as fixation properties of fabric. It appears that the developed reactive dye's structure, which generates the -SO_2NH- bridging group, is encouraging applicants for use in the dyeing and printing of cotton fabric. The introduced of sulfonamide group in synthesized molecules of novel dyes relationship and consequently to developed the exhaust and fixation behaviour of the synthesized dye conceivably a good process for new designing of reactive dyes.



Reactive dyes prepared by Lilli Yang et el

Siddiqua Umme Habibah et al., [50] have been synthesized novel hetero functional azo reactive dyes, for improved fastness properties and exhaust properties sulphatoethylsulphone and triazine is used as chromophoric group for synthesized hetero functional novel azo reactive dyes. Reactive dyes that were created and utilized as standards for compression to Reactive Red-195. The dyes was prepared via condensation and diazotization process. Without distinguishing any particular necessity, the synthesised dyes R1 and R2 were rectified using B3LYP and CAM-B3LYP. Safe equivalency of the advanced geometries resulted in structural similarity in both produced dyes. Because both dyes were made with the addition of the sulfatoethylsulfone group, phenyl diazene, naphthalene disulfonic acid, chloro triazine, and other compounds, they are equal in colour.

Several substituent positions of the sulphato-ethyl-sulfone group along the bridging moiety caused the structural inequality. When applied to cotton fibres, all synthetic dyes produced excellent colouring and wet fastness characteristics.

Shafia Sagheer et al., [51] synthesized sulfonamide based reactive dyes in this series of reactive dyes sulfonamide components used as intermediates. The main object of this study was study of antimicrobial activity, disk diffusion method was used. The synthesized dyes were strong candidates for several textiles' material mostly for medicine and different veterinary materials. The build-up properties of sulfonamide based reactive dyes was also excellent.

Huei-Chin Huang, et al., [52] have been synthesized ten reactive dyes out of these, five are monochloro-s-triazinyl (MCT) dyes and the other five are m-carboxypyridinium-s-triazinyl dyes (NTR), which were created by creating an -NHCN, $-OCH_3$, $-CH_3NSO_2CH_3$, -N-methyl phenyl, or -OH group as the second-leg substituent. The kinetic study of hydrolysis reactive dyes were studied, the higher the electron donating behaviour of the substituent on meta position to the withdrawal group in the triazine ring, the smaller the hydrolysis rate constant. Fatma A. Mohamed et al., [53] have been prepared novel N-amino rhodanine-based bis monofunctional and bifunctional reactive dyes and they were used on wool and cotton fabric. The dyes were synthesized with first condensation m-phenylene diamine sulphonic acid with cyanuric chloride, the second condensation takes place by sulfanic acid or 1-aminobenzene-4-β-sulfatoethylsulfone at room temperature. After that diazotized with sodium nitrite to suitable amine in concentration hydrochloric acid at 0-5 ^{0}C under stirring, after that coupled with component (3-amino rhodamine with glutaraldehyde and terephalaldhyde). Synthesized dyes were applied on cotton and wool fabric resulted excellent fixation values and high light fastness properties. Measure the wool and cotton fabrics' antibacterial effectiveness both against Gram-negative and Gram-positive microorganisms.

1.8. References

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