



## TECHNICAL FACTS & FIGURES OF REACTIVE DYES USED IN TEXTILES

\*Chinta S.K. & Shrivastava VijayKumar

D.K.T.E'S Textile & Engineering Institute, Ichalkaranji, Maharashtra, India

### ABSTRACT

Textile industry comprises of dry mechanical and wet chemical processing, wet chemical process comprises of bleaches, dyeing, printing, & finishing. Dyeing is art of colouration to textiles. Dye get transferred to textile during dyeing. Dyeing operation is performed by the reaction between fiber and dyes. Some dyes are water soluble and some are water insoluble. Some fiber has affinity to dye; some have no affinity to dyes. So dyeing depends on both fiber and dyes chemical properties. Before dyeing we have to consider this factor. The fiber reactive dyes are known as the best for cotton for its wide range of application and better fastness properties. And these dyes are characterized by its reactions between dye and fiber.

**KEYWORDS:** Reactive dyes, dyeing & fixation, hydrolysed dye,

### INTRODUCTION

#### Reactive Dye

Reactive dye is the only class of dyes amongst all the classes of dyes which makes co-valent bond with the fiber and becomes a part of it. This can be described as:

Reactive dyes + Fiber = Reactive dye-Fiber  
(covalent bonding)

If the general structure of a reactive dye is "R-B-X" then,  
R-B-X + Fiber = R-B-X-Fiber (Dyed fiber)

Here,

R = Chromophore Group (Azo, Anthraquinone, Phthalocyanine etc.)

B = Bridging Group ( Imino, Ethyl & Methyl, Oxide, Sulphide group)

X = Reactive Group (-Cl, -Br, -SH, -OCH, etc.)

#### Classification of Reactive Dyes

- By depending on the chemical constitution reactive dyes can be classified as:
  1. Chlorotriazine Dyes (MCT)
  2. Vinyl Sulphone Dyes (VS)
  3. Heterocyclic Helogen Containing Dyes (HHC)
  4. Mixed Dyes (MCT-VS)

- By depending on application methods of temperature, reactive dyes can be classified as:

**Cold brand reactive dyes** This type of reactive dyes is applied at low temperature i.e. at room temperature. They are highly reactive with fiber at this temperature.

**Hot brand reactive dyes** This type of dyes is applied at a medium temperature around are 60°C. Their reactivity is medium with fiber.

**High Exhaust brand reactive dyes** This type of dyes has very low reactivity properties with fiber as against the reactivity with cold and hot brand reactive dyes. Dyeing is carried out around 80-90°C.

#### Properties of reactive dyes

1. Reactive dye is anionic in nature.
2. Reactive dye is a water soluble dye.
3. They have better wash and light fastness properties.
4. They have better substantivity.
5. They form strong co-valent bond with the cellulosic fiber in alkaline condition.
6. The electrolyte is must for exhaustion of dyes in the fiber.
7. A certain amount of dyes is hydrolyzed during application. (around 15-20%)
8. Wide range of color can be produced with reactive dyes.
9. Comparatively cheaper in price.

#### REACTIVE CLASS OF COLOURS

Reactives are the most important class of colours for the dyeing of cotton. Reactive Dyes are capable of forming chemical covalent bonds with the Hydroxyl groups of cellulose fibre and therefore, better anchored to the substrate and not depend on the relatively weak physical forces to give better levels of fastness. The range of colours includes very bright shades - pastel to very dark and also blacks and Navies with reasonable fastness characteristics and costs. Depending on the reactive group/s they constitute- like a triazinyl ring system or vinyl sulphone, they react with the hydroxyl group of cellulose undergoing nucleophilic substitution / take part in addition reaction. The reactivity of the dyes are of following two types.

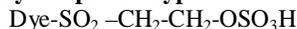
#### Tri-azinyl Type Ring system

By virtue of halogen attachment and the heterocyclic Nitrogen the carbon atom in the Triazinyl ring acquires a positive charge and is subjected to nucleophilic attack by any ionized species.

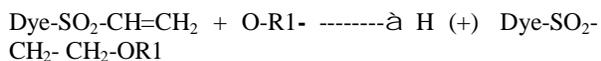


Where R is the dye residue and R1 is the species residue (Cellulose or Water)

### β-Sulphato ethyl Sulphone Type



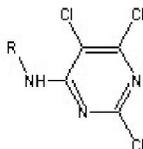
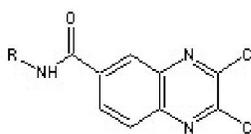
The electron attracting sulphone group causes electron deficiency on the terminal carbon atom enabling nucleophilic attack to take place. (Addition reaction)



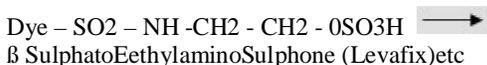
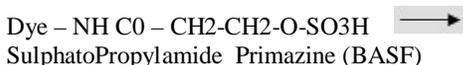
Where [O-R1]- is [Cellulose O -] or [OH -] of water, etc. Remazol is reactive dyes based on Vinyl Sulphone system

Besides Triazinyl /Vinyl Sulphone systems, there are other hetero cyclic Nitrogen ring systems with F / Cl attachment at the Carbon atom. Similarly like in β- Sulphato ethyl Sulphone which causes an electron deficiency in the terminal Carbon atom, other groups that causes similar effect to the end carbon atom have all been exploited to confer different characteristics to the dye's substantivity / reactivity with cellulose.

R is the dye chromophore



2, 3 Di-ChloroQuinoxaline 6 Tri ChloroPyrimidinyl Amino Dyes Carbonyl Amino Dyes LevafixE (Bayer) Reactones (Drimarines -Sancoz/Clariant) (Geigy) Etc.



Linking of the dye chromophores to the reactive groups through different bridging groups modify the various characteristics of the reactive dyes.

### Criteria for Reactivity

It may be noted that the attacking species is an ion and not an uncharged molecule and at neutral pH, necessary nucleophiles are not present for any reaction to take place and therefore the Reactive dyestuff renders itself amenable to be dissolved in water to carry out the absorption and exhaustion part of the dyeing at neutral pH without reacting with fiber. After the satisfactory absorption phase, the pH is raised causing reaction to take place. As the pH increases ionization with Cellulose increases. However beyond specific pH levels dictated by the various reactive systems, the dye absorption slows down due to higher levels of ionization of the cellulose and consequent

competition for the available cations. The effect is greater with low affinity dyes. The role of pH and its control need not be overemphasized.

Water being the competitor for reaction with the dye (hydrolysis), it is still the cellulose fibre that takes part in the reaction due to the following two reasons, which outweigh the preponderance of water in the dye bath and cause fixation of the dye to the fibre to be the preferred course of reaction.

1. The affinity due to the substantivity of the dye to the substrate is greater than that to water and therefore at the end of the exhaustion the dye on the substrate is far greater than that is in the bath.
2. Secondly Cellulose has lower dissociation constant than water resulting in almost 25 folds greater Cellulose-O<sup>-</sup> ions over hydroxyl ions.

Different reactive systems require different levels of alkali / pH / temperature / time etc. for the reaction to take place and therefore the substantivity and stability of the reactive colour can be accordingly engineered to suit the dyeing methods, like Exhaust, Pad batch. Pad bake etc. and Printing styles.

Bi-functional dye systems have two types of reactive groups in their molecule, each one supplementing and complementing the strengths / deficiencies of the other.

### STANDARDIZATION OF THE DYESTUFF

#### Factors influencing Assessment

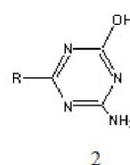
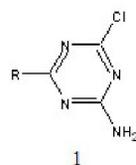
If the colours are fully soluble and follow the Beer Lambert's Law, absorbance measurement of dye solution of a given concentration for all wavelengths would characterize the dye. But due to presence of electrolytes and buffers the dyestuffs do not strictly follow the law and therefore transmission data for colour characterization are likely to mislead. Secondly, the transmission data may be useful for manufacturing activity but the colourant should dye a substrate and therefore the reflectance data after application is more relevant. Also not all colours are 100 %exhaustive on the fibre substrate.

Therefore, dyestuffs cannot be standardized by transmission data alone and the reflectance data are also required. In the case of Reactives, there is one more dimension,ie absorbance measurements of these dyestuffs provide a measure of the chromophoric content only and not the reactive content.

#### Hydrolyzed dye

Both hydrolyzed 'Reactive' dye and the regular Reactive dye will behave very similarly during the absorption /exhaustion phases and exhibit the same absorbance for a given concentration but the un-hydrolyzed one will react with the cellulose and give the desired shade/yield, whereas the hydrolyzed one will not. In the following example it may be noticed one of them has the reactive [Cl] and the other is hydrolyzed [OH]. No.1 will give the desired shade and the No.2 will not.

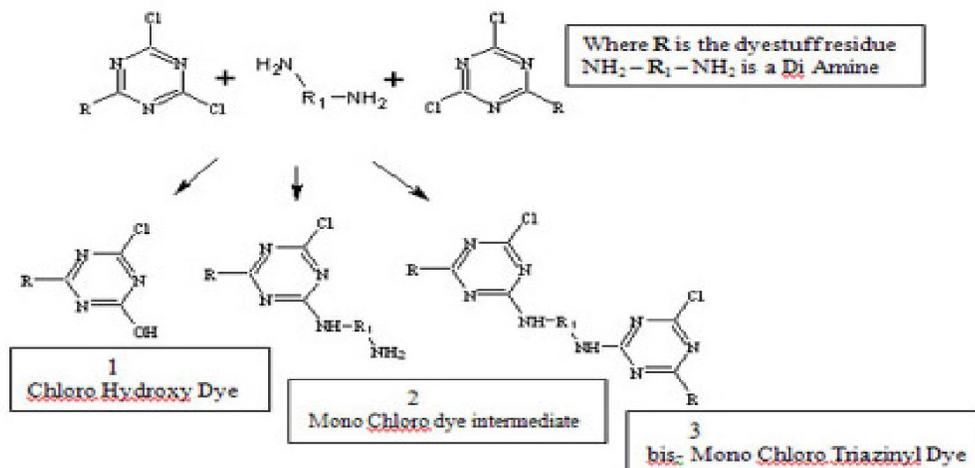
Reactive Species      Hydrolyzed species



Where R is the dyestuff residue

### Impurities' in the Dye

The manufacturing of the dyestuffs involves reactants and the products and that is governed by the process parameters like time, temperature, pressure, concentration etc. -i.e. any variance in these parameters would result in varying degrees of the product yield and the accompanying 'impurities' like unreacted reactants, partially reacted intermediates, salt etc. Depending on the manufacturing techniques and supervision and control, the degree of these 'impurities' would vary. The same generic



The same manufacturer may be able to control and achieve certain level of consistency in the different proportions of the 'impurities' and therefore offer consistency in the performance of the dyestuff, but the same generic colour manufactured by another manufacturer may not be able to maintain the same proportions of the 'impurities' and hence when brands are switched over the problems of shade differences arise. There are also possibilities of presence of isomeric impurities causing different absorbance / reflectance values. The HPLC studies also highlight the different constitutions possessed by the same generic Colour Index dyestuff manufactured by different sources due to complex manufacturing techniques and processes of the different manufacturers. Reactive dyes manufactured by non-standard manufacturers are likely to vary from one manufacturing batch to another. This stresses the need not only to establish the credibility of the source but also retain the *established* source to meet consistency in quality. With the present system of specifications for shade variation based on  $\Delta E$  limits, if the variation in dyestuff itself contributes to a sizable percentage of the  $\Delta E$  tolerance, there is very little that is available for more major contributors in actual dyeing process.  $\Delta E$  tolerance is 1.2. It is reasonable to assume that proper control and discipline can restrict the shade variation in bulk to a  $\Delta E$  tolerance of 0.9 and that gives a margin of  $\Delta E$  0.3 for dyestuff varieties. Statistically it has been shown that dye standardization of  $\pm 2.5\%$  gave an RFT result of 93% (with good discipline in dyeing operation) for  $\Delta E$  tolerance of 1.2, which is liberal. That puts the manufacturer /dye in a more difficult spot. In other words the standardization should be  $< 2.5\%$  and the dye need to be more disciplined to achieve  $\Delta E$  by 1.

colour manufactured by different manufacturers would again contribute to the complexity of the variables.

In the following example, the bis-Mono Chloro Triazinyl dyestuff can have different proportions of the three products, however small, in the final 'dyestuff'. This is because stoichiometric quantities of the (Dye)-Triazinyl and the di amine have not taken part in the reactions. By careful control of the reaction parameters, yield of No. 3 – the required dyestuff would be maximized, but there would still be certain quantities of the other ingredients.

### Moisture in the dyestuff

The other factors would include moisture content that shall not exceed 3.5%. The hydrolysis is accelerated by alkaline pH and hence packing, transportation, storage, handling etc should desist any alkalie contamination.

#### • Selection of Colours

Selection of colours is an important exercise and slackness in this aspect can cause problems despite taking care of other factors/ variables. The dyestuffs not only should belong to the same group of the reactive class but also possess similar substantively / exhaustion and reactivity characteristics- i.e. the dyes selected should have very close exhaustion and reactivity curves. Where the dyestuff has a high exhaustion and relatively low reactivity the dye exhausted would continue to wash off with any number of soapings, as the same is not fixed. Such a situation can also happen if the dyestuff is partially hydrolyzed due to reasons already discussed. In a tertiary match with three colours, the role of such dyestuffs with mismatched characteristics can cause undue problems of the unfixed colours washing off to different extents causing a significant variation in the end shade. Very high and very low reactivity factors of dyestuffs in a recipe can cause fixation problems.

#### • Control of variables

There are quite a number of variables that require more careful and special treatment and others that are less difficult to manage.

#### Variables those are readily manageable

The dyestuff, water, quality of chemicals, material handling, weighment accuracy, dyeing sequence, and machinery and methods may be standardized as they are specification or system based activities and can be

managed by strict discipline - to that extent we have lesser number of variables to address.

**Water**

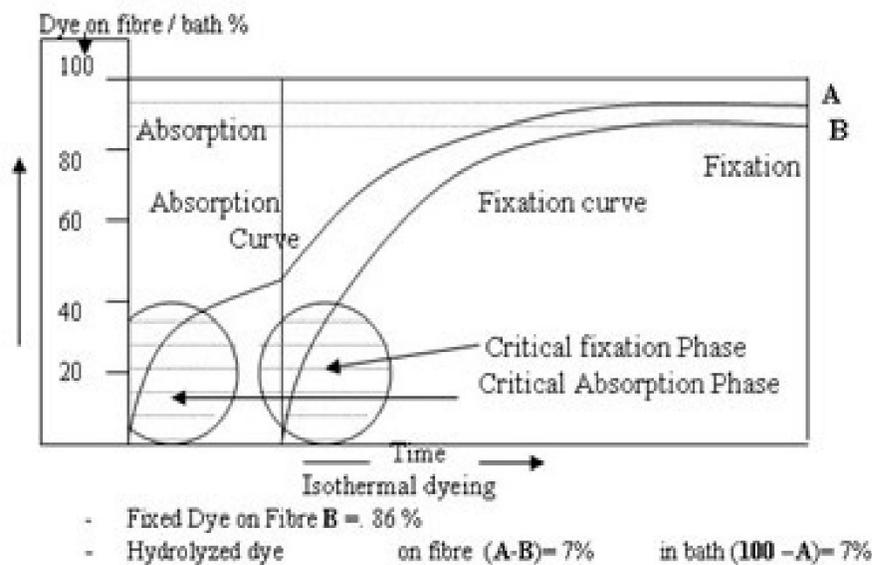
Quality of water can be corrected by standard processes and brought to the required norms. Water hardness and iron contamination are not conducive to dyeing and therefore the water has to be treated for hardness and iron. 'Ca<sup>++</sup>' and 'Mg<sup>++</sup>' should not be present as they would interfere with the solubility of the dye forming Ca and Mg compounds of the dyes. Secondly use of the common sequestering agents of the type EDTA, EDTMP would not only sequester the Ca and the Mg hardness but also metal complex in the dyestuff itself invariably Cu. It would be therefore recommended to remove the Ca and, Mg hardness in the water. It would be advantageous to use special sequestering agents that would not disturb the stability constant of the Cu with the relevant dyestuff but only would sequester the Ca and Mg. This addition is recommended because the Ca and Mg contamination could come from the substrate of the other chemicals used. Summing up the factors that are readily manageable.

**Variables those are more difficult to manage**

The process variables of temperature, time, concentration / dozing etc. require dynamic monitoring and control - activities that are difficult to perform manually. These

variables need to be dealt with tools and methods that are specific for each of the variables. The dyeing system may demand a particular temperature / time profile or different dozing profiles. The pH profile is another factor that can derail the course of a dyeing. The absorption phase is dependent on the substantivity and dyestuffs with very low and high substantivities in a recipe will cause problems of uneven dyeing and shade variation, unless guarded by addition of specialty chemicals that even out the dye uptake.

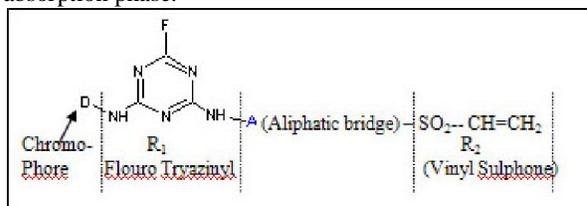
The absorption phase is very critical, where the curve is steep and dyestuff would rush causing uneven application. This is compounded by the addition of electrolyte for exhaustion purposes. During the addition of electrolyte, if not evenly controlled the salt concentration may exceed at times and aggregation of the colour can take place, which would cause deposition of colour on the substrate in clusters causing skittery dyeing. While common salt can be freely soluble unaffected by an increase in temperatures whereas Glaubers salt solubility decreases at higher temperatures. These are difficult to manage manually and dyeing systems employing PLC controlled dosing or addition of specialty chemicals that prevent dyestuff aggregation which are available and they need to be used.



In the fixation phase, the alkalis used and their concentrations are critical. The temperature and the alkali chosen would depend on the reactivity of the dyestuffs in the recipe and the pH parameter need to be carefully controlled and maintained over the fixation period.

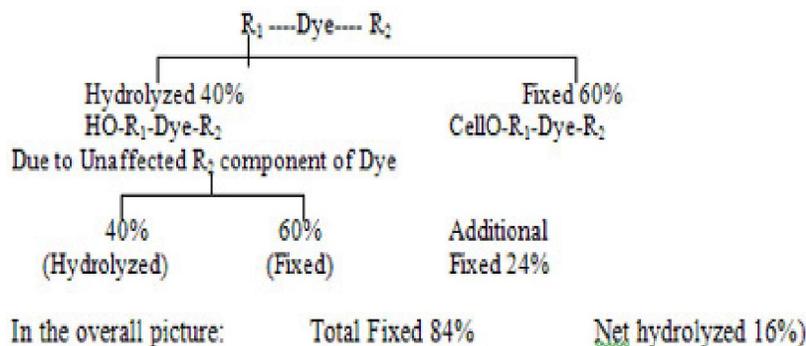
The degree of levelness of a reactive dye depends on the tolerable amount of dye, which is bonded to the fibre per bath material contact; beyond this limit the dyeing is uneven. There is a critical phase when the rate of fibre dyestuff bonding is accelerated and pH level (alkali levels) need to be controlled in this zone for even results. It should also be borne in mind that linear addition of alkali does not result in corresponding linear development of pH. On the other hand higher pH would induce exhausted dye to hydrolyze. The variance in pH needs to be within 0.35 units against the desired levels.

Bi-functional dyes and low salt system have been developed for better levels of fixation and lower ecological disturbances. The advantages of both the Triazine and Vinyl Sulphone systems are exploited. Bi-functional dyes with the two reactive systems in the dye molecule tend to have the best of both (higher affinity due to the 'Triazinyl' and lower affinity due to the 'Vinyl Sulphone') and therefore more controllable during the absorption phase.



Also the fixation due to the two reactive systems one occurring faster --mono Chloro or Flouro Tri-azinyl (higher reactivity) followed by the slower second one-- the Vinyl Sulphone (medium reactivity) with stable dye fibre

bond. The fixation through the first system is supplemented by the fixation through the second system and thus an overall fixation level of over 80% is achieved as represented in the following example.



With suitable reactive systems even higher fixation levels are possible due to both nucleophilic substitution (Tri-azinyl) and addition (Vinyl Sulphone) bonds, the fastness characteristic and resistance to acid, alkali and peroxide are improved.

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