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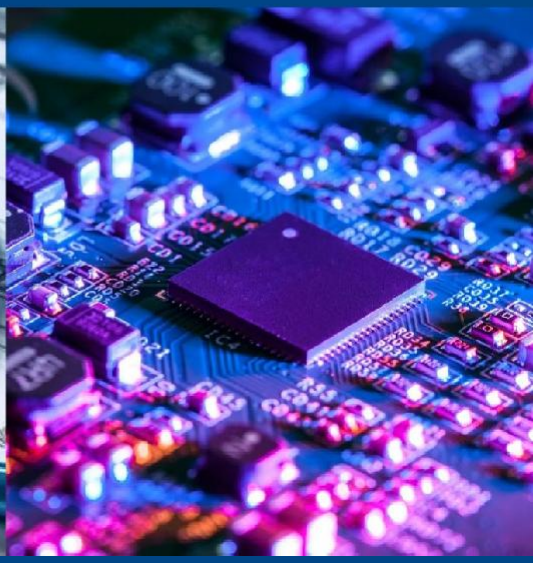

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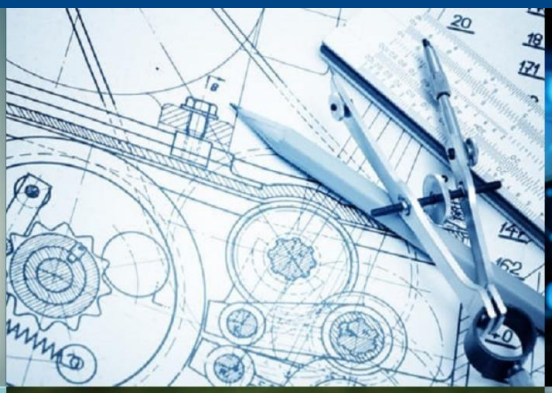

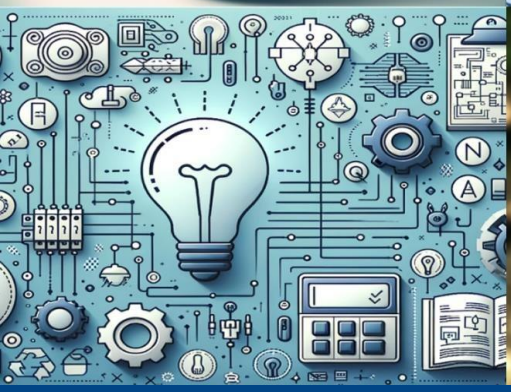

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# Classification and Properties of Reactive Dyes used in Textile Industry

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**ABSTRACT:** Almost every color can be produced using synthetic dyes, which are frequently used in many different sectors for printing and dying. Because of their excellent fastness to wet treatment, reactive dyes are among the most widely used and safest synthetic dyes in the textile industry. With several reactive groups, it is one of the most well-known and often used kinds of reactive dye. It is primarily categorized according to its dyeing temperature, reactivity, and reactive group. Different reactive dyes with different reactive groups of reactive systems are also available that react with the substrate to produce covalent bonds. This bond formation between the functional group and the substrate results in high wet-fastness properties. They are capable of forming bonds with active sites in fibers such as hydroxyl groups in cellulose, amino, thiol, and hydroxyl groups in wool and amino groups in polyamides under alkaline conditions. They are manufactured from a combination of many structural dyes to get certain hues. These dyes are simple to use and widely useful in a variety of applications, including printing, continuous dyeing, exhaust dyeing, and more.

**KEYWORDS-** Classification, Covalent Bond, Reactive dyes, Reactive group, Safest dyes, Synthetic dyes

## I. INTRODUCTION

Reactive dyes are the most popular dyes used in the textile industry. It also considered as one of the safest dyes that offers broad color spectrum and a higher fastness in application with affordable price. (Khatri et al., 2015; Lewis, 2011). Reactive dyes are coloured compounds that contain various reactive (functional) groups with various reactive systems that react with substrate to form covalent bonds. These dyes are easy to use and applicable extensively in various fields such as exhaust dyeing, continuous dyeing and printing, etc.

Reactive dyes have many advantages such as treated at mild conditions, give bright colors and stable structures. The origin of the term “reactive dyes” comes from their ability to create a covalent bond with active sites in fibers such as hydroxyl groups in cellulose, amino, thiol, and hydroxyl groups in wool and amino groups in polyamides under alkaline conditions (Burkinshaw & Salihu, 2018, Panda H. 2021). These dyes are nitrogen containing hetero cyclic rings carrying halogen substituents, therefore undergo nucleophilic substitution reaction with the cellulose fiber. The hetero atom activates the system for nucleophilic attack due to its electro-negativity. The attacking nucleophile can be either a cellulose anion or a hydroxyl ion. This conducts fixation on the fabric, after hydrolysis occurs on the reactive dye and it is also important for a dye molecule to have a high dye fabric covalent fixation value (Gowri, et al., 2014).
This bond formation between the functional group and the substrate results in high wet-fastness properties. These dyes differ fundamentally from other types of dyes that owe their wet-fastness to physical adsorption or mechanical retention. The main objective of dyeing and printing with reactive dyes is to obtain the maximum fixation and minimum hydrolysis with water. The smaller the amount of hydrolysed dye, the easier will it be in the final washing operation. The principal commercial applications of reactive dyes are in the dyeing of cellulose, wool, and nylon, either individually or as components of fiber blends. They have also found use in dyeing silk, hair, and leather (Panda H. 2021).

Generally, some synthetic dyes are naturally toxic but due to the high fastness and washing off characteristics of reactive dyes, the risk of dye toxicity decreases significantly. There have been zero allergy cases reported due to textile products dyed with reactive dyes (Hunger & Sewekow, 2002). However, studies are still done to further improve the utilization of reactive dyes, especially on how to effectively apply them to synthetic fibers, further improving the

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variability of the color (H. Zhang et al., 2021), developing low-salt content dyes to reduce the environmental burden (Khatri et al., 2015), and giving additional function other than to color the textile products.

**Classification of reactive dyes:**

It is mainly classified on the basis of their reactive group of reactive system, reactivity and dyeing temperature as shown in **Figure 1** (Chinta & Kumar, 2013, Kamińska et al., 2020, Kiron, 2021, Panda H. 2021, Koushik and Josico, 2003):

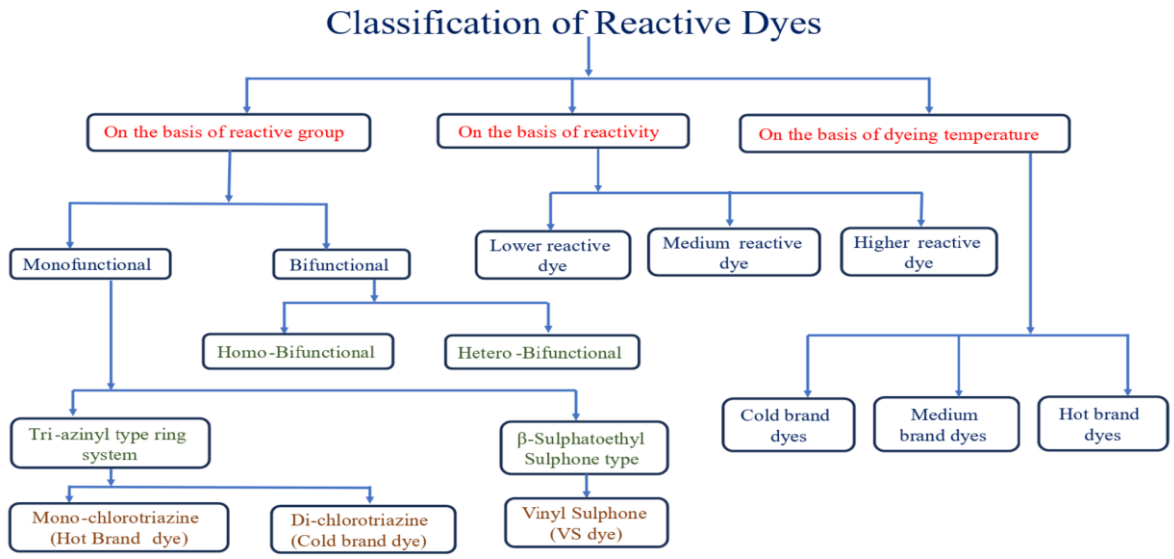


**Figure1.** Classification of reactive dyes used in textile industry

## II. ON THE BASIS OF REACTIVE GROUP

**(a) Monofunctional reactive dyes**

These dyes are characterised by the presence of reactive groups (one or two reactive species) at individual locations in the dye molecule. All the reactive dyes developed during the early stages of development were monofunctional reactive dyes. Typical examples of this kind of dyes having monochloro and dichlorotriazine of tri-azinyl type ring system and vinyl sulphone of β-sulphatoethyl sulphone type reactive groups. Although dichlorotriazine dyes contain two reactive chlorine atoms, located on the same triazine ring considered as monofunctional reactive dyes.

**1) Tri-azinyl type ring system-** These dyes are made from cyanuric chloride, in which the replacement of each successive chlorine atom is increasingly difficult. The first one is reactive even in the cold, the second one at room temperature and above, while the third requires refluxing in aqueous solution or under anhydrous conditions at higher temperatures. Dyes such as Procion (ICI), Drimarene (Clariant), Levafix E (Bayer) and Cibacron (Indo-Swiss) derivatives are used in this group of reactive dyes. These dyes react with cellulose and form an easter linkage with the fibre by a process called nucleophilic substitution (Koushik and Josico, 2003).

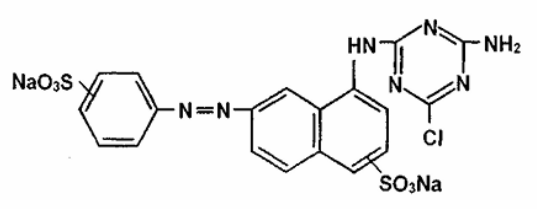


**Figure2.** Structure of triazine reactive dyes

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**i) Monochlorotriazine reactive dye -** When two of the three chlorine atoms of the cyanuric chloride are replaced by a dye and suitable amino compound, the resulting dye is left with only one chlorine atom, which is much less reactive. Dyes based upon this reactive group would require higher temperature for fixation because the reaction with cellulose has been carried out at higher temperatures and such dyes are marketed as hot dyeing or H brand reactive dyes. Structure of the Procion H dyes (hot brand dye) shown in **Figure 3** (Koushik and Josico, 2003).

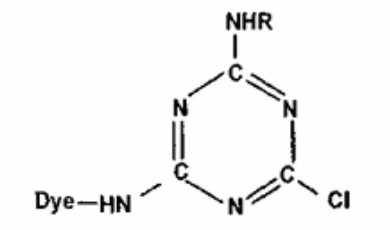


**Figure3.** Structure of Monochlorotriazine reactive dyes

**ii) Dichlorotriazine dyes –** Only one of the two chlorine atoms of a dichlorotriazine dye is reacted with cellulose by nucleophilic substitution at room temperature and some portion of the dye reacts with hydroxyl group of water molecules simultaneously leading the formation of hydrolysed dye which cannot react with cellulose because other requires temperatures above 60°C for the reaction. Procion M dyes, which have as the reactive centre a dichloro-S-triazine group, are the most reactive and therefore the dyeing reaction takes place in the presence of an alkali even in the cold and at room temperature hence they are called cold dyeing or cold brand reactive dyes. The structure of Procion M dyes (cold brand dye) shown in **Figure 4** (Koushik and Josico, 2003).

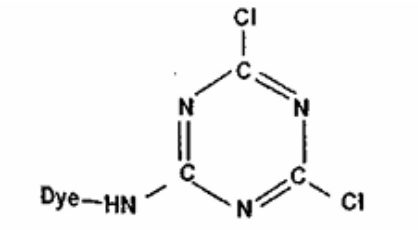


**Figure4.** Structure of Dichlorotriazine reactive dyes

**2) β-Sulphatoethyl sulphone type-** These dyes react with cellulose by the mechanism of nucleophilic addition i.e. etherification. The reactivity of this dye lies between those of monochloro and dichlorotriazinyl dyes. The Remazol dyes (Dye-star), Levafix dyes (Bayer) and Primazin dyes (BASF) come under this group of reactive dyes.

**i) Vinyl sulphone (VS-brand dyes)-** Vinyl Sulphone dyes are reactive dyes containing a sulphatoethyl sulphone group in the molecules, first introduced by Bayer in Germany. The formation of vinyl sulphone from sulphatoethyl sulphone takes place by addition of alkali, which reacts with hydroxyl group of cellulosic fibres by a process called nucleophilic addition and form an ether linkage with the fibre. Reactive dyes having a vinyl sulfone group have excellent light and washing fastness. These dyes have good stability under neutral and acidic conditions but poor stability under alkaline conditions. These dyes are mainly used in the dyeing and printing of cotton textiles (Panda H. 2021).

**(b) Bifunctional reactive dyes** - Bifunctional reactive dyes and low salt reactive dyes were developed more recent for producing better fixation of dye and to reduce environmental problems. These dyes are characterised by the presence of two reactive groups of same type (mono or dichloro triazine) or two different types (monochloro triazine and vinyl sulphone) at two different locations in the dye molecule. These dyes are further classified as homo-bifunctional and hetero-bifunctional dyes. The various bifunctional combinations that can be formed are listed below in **Table 1** (Koushik and Josico, 2003).

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**Table1.** Various combinations of bifunctional dyes

| | | |
|---|---|---|
| MCT/MCT | Monochlorotriazine/Monochlorotriazine | Homo-bifunctional |
| VS/VS | Vinylsulphone/Vinylsulphone | Homo-bifunctional |
| MCT/VS | Monochlorotriazine/Vinylsulphone | Hetero-bifunctional |
| FT/VS | Fluorotriazine/Vinylsulphone | Hetero-bifunctional |
| FCP/VS | Fluorochloropyrimidine/Vinylsulphone | Hetero-bifunctional |

**1) Homo-bifunctional reactive dyes-** Homo-bifunctional dyes having two reactive systems of the same type (triazine or vinyl sulphone). The concept of dyes with two reactive systems of the same type were developed for exhaust dyeing having higher substantivity and better exhaustion and fixational compared to the mono-functional dyes. The dye-to-fibre bond is stable to mild acids and alkalis. Procion HE and Procion H-EXL dyes are example of a homo-bifunctional reactive dye is shown in **Figure 5** (Koushik and Josico, 2003).

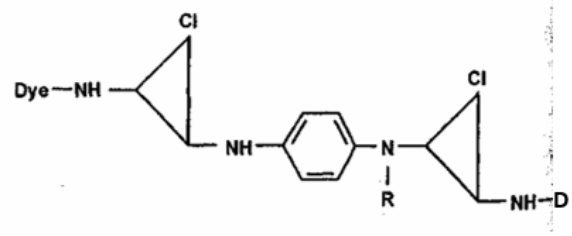


**Figure5.** Structure of Procion HE and Procion H-EXL reactive dyes

**2) Hetero-bifunctional reactive dyes-** Hetero-bifunctional having two reactive systems of the mixed type (triazine-vinyl sulphone). Bifunctional dyes with mixed reactive system in the dye molecule possess the advantages of both the triazine and vinyl sulphone system. The triazinyl group (higher reactivity) reacts with the fibre faster due to higher affinity of triazinyl and this is followed by the reaction of vinyl sulphone (medium reactivity) which is slower in forming a stable dye-fibre bond due to the lower affinity of Vinyl sulphone. Sumifix supra dye is example of a hetero-bifunctional reactive dye is shown in **Figure 6** (Koushik and Josico, 2003).

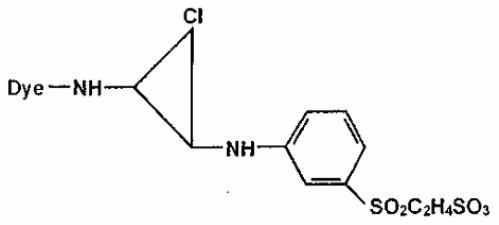


**Figure6.** Structure of Sumifix supra reactive dyes

## III. ON THE BASIS OF REACTIVITY

Reactive dyes possess high, moderate and low reactivity. An ideal reactive dye is those which has high reactivity with cellulose and at the same time having good stability in alkaline solutions or pastes. Generally, the greater the reactivity of the dye, the greater is its instability in alkaline medium. This type of dyes lies in three categories as mention below (Panda H. 2021):

**a. Lower reactive dye:** A low reactivity product requires a strong alkali like Sodium Hydroxide (NaOH) to maintained pH 12-12.5 in dye bath.

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**b. Medium reactive dye:** A moderately reactive dye requires an alkali such as Sodium Carbonate ($Na_2CO_3$ or Soda ash) to maintained pH 11-12 in dye bath.

**c. Higher reactive dye:** A highly reactive dye which combines with the fibre rapidly or hydrolyse in water in a short period of time requires only weak alkali such as sodium bicarbonate ($NaHCO_3$) to maintained pH 10-11 in dye bath.

## IV. ON THE BASIS OF DYEING TEMPERATURE

**a. Cold brand dye**

Cold brand reactive dye contains reactive group of high reactivity than hot-brand reactive dyes. In this type of dye, two chlorine atoms are present in the dye molecule, one of the chlorines is so reactive, which highly react with cellulose fibers even at the room temperature. For dyeing, dye stuff should be first dissolved in water at 30-50 °C and should not be boiled (Singh & Sheikh, 2022, Shenai, 1977). PROCION M, PROCION MX, PROCION ME, LIVAFIX E and Dylon Cold are the examples of cold brand dye (Kiron, 2021, Kiron, 2015, Ahmed, 1995, Gowri et al. 2014). Some other examples of this brand dyes shown in **Table 2** (Panda H. 2021).

**Table2.** Popular cold brand reactive dyes used for commercial purpose

| No. | Commercial Name | C. I. Generic Name | Constitution | Remark Hue |
|---|---|---|---|---|
| 1. | Brill. Yellow 4G | Reactive Yellow 4 | Monoazo Reactive system Dichlorotriazinyl | Bright Reddish Yellow |
| 2. | Yellow RG | Reactive Yellow 7 | Azo Reactive system Dichlorotriazinyl | Bright Reddish Yellow |
| 3. | Yellow 4R | Reactive Orange 14 | Monoazo (Pyrazolone) | Bright Reddish Orange |
| 4. | Brill. Orange 2R | Reactive Orange 4 | Azo Reactive system Dichlo-rotriazinyl | Bright Reddish Orange |
| 5. | Brill. Red EBN | Reactive Red 2 | Monoazo Reac-tive System Dichlorotriaznyl | Bright Bluish Red |
| 6. | Brill. Rose 3B | Reactive Red 11 | Azo Reactive System Dichlorotriazinyl | Bright Bluish Red |
| 7. | Brill Pink B | Reactive Red 74 | Azo | Bright Bluish Red |
| 8. | Brill. Magenta B | Reactive Violet 13 | Azo | Bright Reddish Violet |
| 9. | Brill. Violet RR | Reactive Violet 14 | Dichlorotriazinyl | Bluish Violet |
| 10. | Brill. Blue R | Reactive Blue 4 C.I. NO. 61205 | Azo Anthraquinone Reactive system | Bright Blue |
| 11. | Navy Blue 3 R | Reactive Blue 9 | Azo (Copper complex) Reactive System-Dichlorotriazinyl | Reddish Navy |

**b. Medium brand dye**

Medium brand dye contains reactive groups of moderate reactivity with fiber. When only one chlorine atom is present in the dyestuff molecule, the reactivity of the dye decreases. Because of that this type of dye is applied at a medium temperature of around 50-70 ºC. In this type of dyeing, the solution is prepared by mixing the dye stuff with a little

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warm water, adding the requisite quantity of hot water, and boiling the solution for a short while. Sodium bicarbonate used as the alkali gives maximum color value (Shenai, 1977). Remazol and Livafix are the examples of medium brand dye (Kiron, 2021, Ahmed, 1995, Gowri et al. 2014).

**c. Hot brand dye**

Hot brand dye contains reactive groups which has very low reactivity properties with fiber as compared to the reactivity of cold and medium brand reactive dyes. So high temperature is required for dyeing around 70-90 °C. The exhaustion is affected by the addition of Glauber's salt and the fixation of soda ash. When soda ash is used as the fixing agent, the temperature of the dye bath should not be below 80 °C (Chinta & Kumar, 2013). PROCION H, PROCION HE and CIBACRON are the examples of hot brand dye (Kiron, 2021, Kiron, 2015, Ahmed, 1995, Gowri et al. 2014). Some other examples of this brand dyes shown in **Table 3** (Panda H. 2021).

Apart from these dyes, Sunitomo Chemical Co., of Japan have developed some new hot brand dye under the trade name 'Sumifix' and Sumifix Supra', which can be applied to cellulose, silk, etc. The dyes are enlisted in the **Table 4** (Panda H. 2021).

**Table3.** Popular hot brand reactive dyes used for commercial purpose

| No. | Commercial Name | C.I. Generic Name | Constitution | Remark Hue |
|---|---|---|---|---|
| 1. | Brill. Yellow4G-X | Reactive Yellow 18 | Monoazo (pyrazolone) monochloro-triazinyl | |
| 2. | Bright Greenish Yellow | Yellow R-X Reactive Yellow 46 | Azo | Bright Reddish Yellow |
| 3. | Golden Yellow IR | Reactive Orange 12 | Monoazo | Yellowish Orange |
| 4. | Brill. Orange R | Reactive Orange 37 | Azo | Bright Reddish Orange |
| 5. | Brill. Orange 2R | Reactive Orange 13 | Monoazo | Reddish Orange |
| 6. | Brill. Red 6B | Reactive Red 76 | Azo | Bright Bluish Red |
| 7. | Brill. Red 8 B | Reactive Red 31 | Azo | Bluish Red |
| 8. | Brill. Violet 3R | Reactive Violet 1 | Azo (Copper Complex) system Mono-chlorotriazinyl | Bright Violet |
| 9. | Red Brown 4R | Reactive Brown 9 | Monoazo (Chromium-complex) | Bordeaux |
| 10. | Turquoise Blue A | Reactive Blue 71 | Phthalocyanine | Greenish Blue |
| 11. | Turquoise Blue 2-G-X | Reactive Blue 3 | Phthalocyanine | Bright Greenish Blue |
| 12. | Turquoise Blue G | Reactive Blue 25 | Phthalocyanine | Greenish Blue |
| 13. | Navy Blue R | Reactive Blue 59 | Azo | Reddish Navy |
| 14. | Black GR-X or Black HN | Reactive Black 8 | Monoazo (Metal complex) | Bluish Grey |

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**Table4.** Some new hot brand reactive dyes

| No. | Commercial Name | C.I. Generic Name |
|---|---|---|
| 1. | Sumifix Supra Yellow 3RF | Reactive Y-145 |
| 2. | Sumifix Supra Brill. Red 2BF | Reactive R-194 |
| 3. | Sumifix Supra Brill. Red 3BF | Reactive R-195 |
| 4. | Supra Navy Blue 2GF | Reactive B-194 |
| 5. | Yellow FGS | Reactive Y-115 |
| 6. | Yellow GNS | Reactive Y-115 |
| 7. | Yellow GR Special | Reactive Y-116 |
| 8. | Brill. Scarlet R | Reactive R-113 |
| 9. | Brill. Red G | Reactive R-112 |
| 10. | Brill. Red B | Reactive R-111 |
| 11. | Navy Blue GS 15% | Reactive B-147 |
| 12. | Turquoise Blue BF | Reactive B-148 |

## V. ADVANTAGE AND LIMITATIONS OF REACTIVE DYES

The reactive dyes give a better performance than most of the nonreactive dyes. Their advantages over the other dyes are as follows (Panda H. 2021):

**a. Their advantages over vats:**

i) Improved surface appearance and penetration
ii) Avoidance of reduction and oxidation processes
iii) Lower cost
iv) Better range of shades

**b. Their advantages over azoics are:**

i) Better rubbing fastness
ii) Reproducibility of matchings
iii) Better range of shades

**c. Their advantages over pigments are:**

i) Better workability and less scumming of reserved portions
ii) Much better penetrations and much better rubbing fastness even at higher concentrations
iii) Absence of adverse effect in final handle

**d. Their advantages over rapid fasts and rapidiogens in printing are:**

i) Brighter prints and better (softer) handle
ii) No acid steaming for fixation

**Major factors influencing the dyeing behaviour of reactive dyes are:**

**a.** The chemical reactivity of reactive dyes.
**b.** Influence of diffusion and affinity in reactive dyeing of cellulose.
**c.** Reaction between reactive dyes and cellulose.
**d.** Variation of reactive system in reactive dyes.

## VI. ACUTE TOXICITY OF REACTIVE DYES

Human toxicity of textile dyes can be considered in terms of acute toxicity and chronic or genotoxicity. The main problems of acute toxicity with reactive dyes are skin irritation and skin sensitization, caused by oral ingestion and inhalation. It can cause problems to the workers involved in the manufacturing of the dyes and workers who handle the

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dyes in the dyeing process. The chance of exposure to these dyes should be reduced by avoiding dye dust. This may be achieved by using liquid dyes, the minimum dusting formulas, and the use of the suitable personal safety equipment. Reactive dyes have completely different toxicological properties after dyeing and fixation, because the reactive group is no longer present and the high wash fastness of the dyed fabric ensures that no dye is exposed to the skin of the wearer. Consequently, no cases of allergic reactions have been reported by consumers wearing textiles dyed with reactive dyes. The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) has indicated few reactive dyes (shown in **Table 5)** that lead to respiratory or skin sensitization among the workers through exposure (Chavan, 2013, Choudhury, 2018).

**Table5.** Reactive dyes classified as respiratory/skin sensitizers

| Sr. no. | Dyes | CI Names |
|---|---|---|
| **a.** | Yellow dyes | Reactive Yellow 25, Reactive Yellow 39, Reactive Yellow 175 |
| **b.** | Orange dyes | Reactive Orange 4, Reactive Orange 12, Reactive Orange 14, Reactive Orange 16, Reactive Orange 64, Reactive Orange 67 Reactive Orange 86, Reactive Orange 91 |
| **c.** | Red dyes | Reactive Red 29, Reactive Red 65, Reactive Red 66, Reactive Red 123, Reactive Red 219, Reactive Red 225 |
| **d.** | Violet dye | Reactive Violet 33 |
| **e.** | Blue dyes | Reactive Blue 114, Reactive Blue 205 |
| **f.** | Black dye | Reactive Black 5 |

## VII. CONCLUSION

Synthetic dyes, widely used in various industries for dyeing and printing, produce almost every color available in the market today. Among the synthetic dyes, reactive dyes are considered one of the most popular and safest dyes used in the textile industry because of their high fastness to wet treatment. It is one of the prominent and widely used types of azo dye with different reactive groups. It is mainly classified on the basis of their reactive group, reactivity, and dyeing temperature. There are different types of reactive dyes also available with various reactive groups (i.e., with various reactive systems that react with the substrate to form covalent bonds). They can react with cellulose and form covalent bonds. In order to obtain some particular colors, they are made from a mixture of several different structural dyes (reactive groups). These dyes are easy to use and applicable extensively in various fields such as exhaust dyeing, continuous dyeing, printing, etc.

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