The exhaust technique is the most common method for application of reactive dyes as it is resistant to small changes of system variables. It comprises two steps: exhaustion and fixation. During exhaustion the dyes are exhausted from the dyebath and come into the fibre phase.

Terms Used in Direct Exhaust Dyeing

Exhaust method

In the exhaust method, the dye is transported to the substrate by the dye liquor's motion. The dye is **adsorbed onto the fiber surface and ideally diffuses into the whole of the fiber**. **Water consumption** in exhaust application is **higher** than the continuous dyeing method. There are three corresponding ways of dyeing with the exhaust method.

1. **Liquor circulating**: loose stock, sliver, tow, yarn or fabric, is packed into canisters, wound onto cones or perforated beams and placed inside the dyeing vessel. In this way the liquor is pumped and revolves through the material which is stationary.
2. **Material circulating**: Fabric **winch dyeing and jiggers** are the few forms in which material remains in motion and liquor stationary. In this the material moves through the stationary liquor.
3. **Liquor and material both in motion**: **Jet dyeing and soft flow dyeing** application methods where material and liquor both remain in motion.

Continuous method

In continuous method dye is transported to the substrate by passing it through the different stages but continuously. The continuous method is an innovative method where many discrete dyeing stages are combined, such as applying color, fixation and, washing off of unfixed dyes. Types of continuous dyeing are as follows--

1. **Pad –dry – pad steam process**
2. **Pad – dry – steam process**
3. **Pad – steam process etc.**

Exhaustion:

It is defined as the proportion of **dye absorbed by the fiber** in the relation to that **remaining in the dye bath**. It is expressed in terms of a percentage. For example, if

the exhaustion of the dye bath is 50% then it means that 50% of the dye in the dye bath has moved from the dye solution into the fiber.

Fixation:

In textile manufacturing, "**Fixation**" refers to the **process of setting dyes or pigments in the fibers or fabrics** to make them **permanent and resistant to fading or bleeding**. It is an essential step in the dyeing and printing processes to ensure that the **colors remain vibrant and durable over time**.

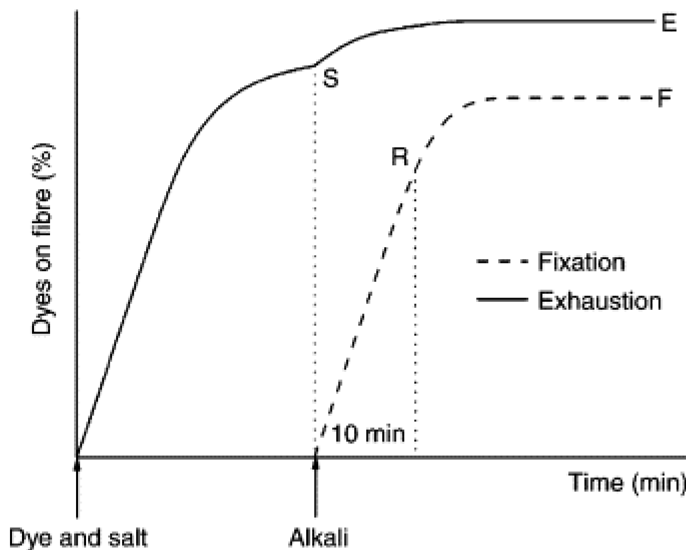


Fig. Dye Exhaustion & Dye Fixation Profiles

There are several methods commonly used for fixing in textile manufacturing:

1) Heat Setting: This method involves subjecting the dyed or printed fabric to **elevated temperatures** to aid in the **chemical reaction between the dye molecules and the fibers**. Heat setting can be achieved through **dry heat methods** like **hot air ovens or steam processes** that involve moist heat. The heat helps the dye molecules **penetrate and bond with the fibers**, resulting in improved colorfastness.

2) Chemical Fixatives: Chemicals known as **fixatives or mordants** are applied to the fabric to improve dye retention and fixation. Fixatives work by **forming complexes with the dye molecules**, enhancing their **affinity** for the fibers. Common fixatives include **metallic salts like aluminum sulfate or potassium alum**, which are used for natural dyes, as well as synthetic fixatives specifically developed for different types of dyes.

3) Reactive Dye Fixation: Reactive dyes, widely used in textile printing, require a different fixing process. These dyes contain reactive groups that chemically bond with the fibers when exposed to specific conditions, such as **heat or alkaline pH**. Fixation of reactive dyes typically involves **steam or hot water treatment**, which activates the reactive groups and ensures a strong bond between the dye and the fabric.

Dyeing Mechanism of Reactive Dye

The dyeing mechanism of material with reactive dye takes place in 3 stages: -

1. Exhaustion of dye in presence of electrolyte or dye absorption.
2. Fixation under the influence of alkali.
3. wash-off the unfixed dye from material surface.

1. Dye absorption:

When fiber is **immersed in dye liquor**, an **electrolyte** is added to assist the **exhaustion** of dye. Here **NaCl** is used as the electrolyte. This electrolyte **neutralizes the negative charge** formed in the fiber surface and **puts extra energy** to increase dye absorption. So when the textile material is **introduces to dye liquor** the dye is **exhausted** on to the fiber.

2. Fixation:

Fixation of dye means the r**eaction of reactive group of dye with terminal –OH or-NH_2 group of fiber** and thus forming strong **covalent bond** with the fiber. This is an important phase, which is controlled by **maintaining proper pH** by adding alkali. The alkali used for this purpose **depends on brand of dye and dyeing temperature**. Here generally **caustic soda, soda ash or $NaHCO_3$** is used as alkali depending upon **reactivity of dye**. They create proper pH in dye bath and do as the dye-fixing agent. The reaction takes place in this stage is shown below: -

$$D\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}OSO_3Na + OH\text{-}Cell = D\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}Cell + NaHSO_3$$

3. Wash-off:

As the dyeing is completed, a good wash must be applied to the material to remove extra and unfixed dyes from material surface. This is necessary for level dyeing and

good wash-fastness. It is done by a series of hot wash, cold wash and soap solution wash.

Process Curve:

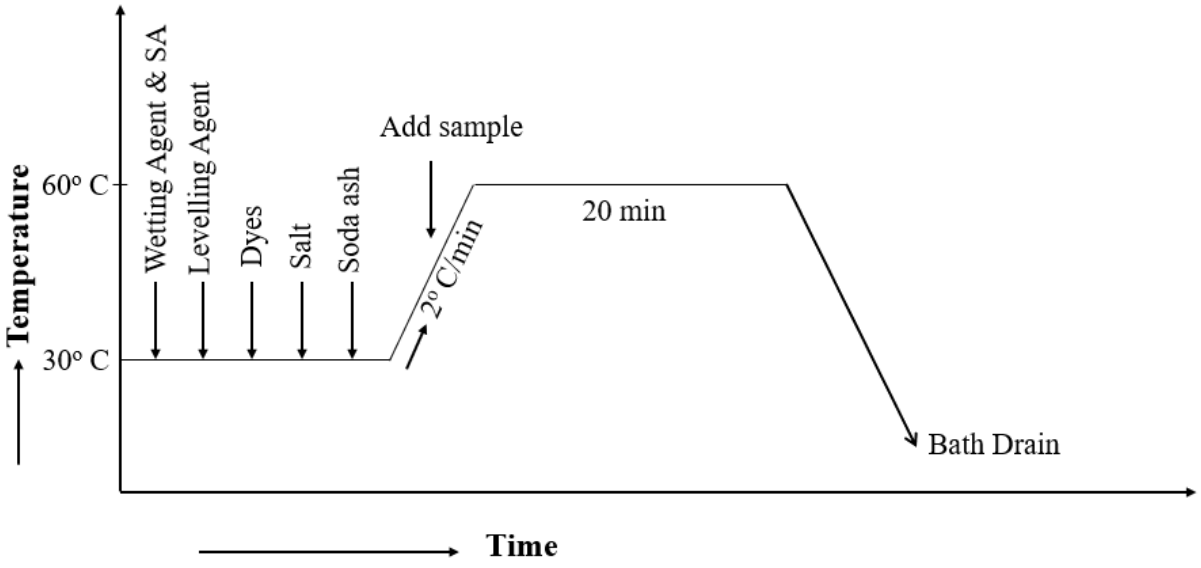
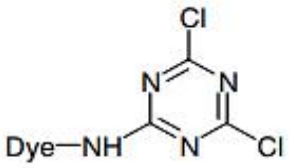
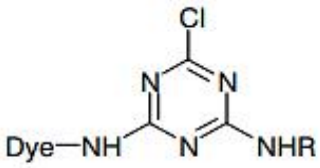


Figure: Dyeing Curve with Reactive Dyes

Mono Functional Reactive dyes

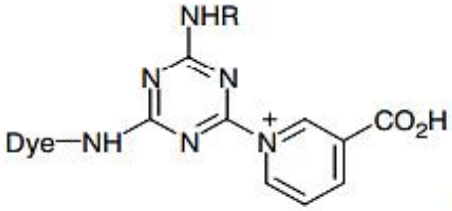


Dichlorotriazine (DCT)

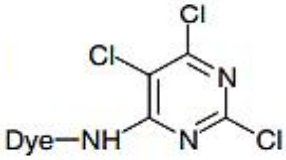


Monochlorotriazine (MCT)

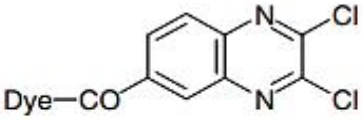
Monofluorotriazine (MFT)



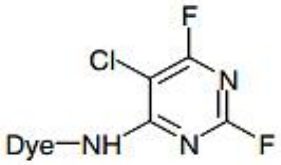
Nicotinyltriazine (NT)



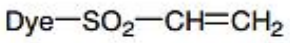
Trichloropyrimidine (TCP)



Dichloroquinoxaline (DCQ)

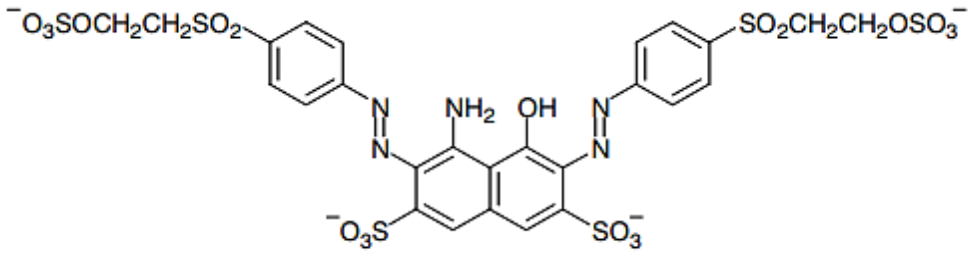


Difluorochloropyrimidine (DFCP)



Vinylsulphone (VS)

Bi Functional Reactive Dyes



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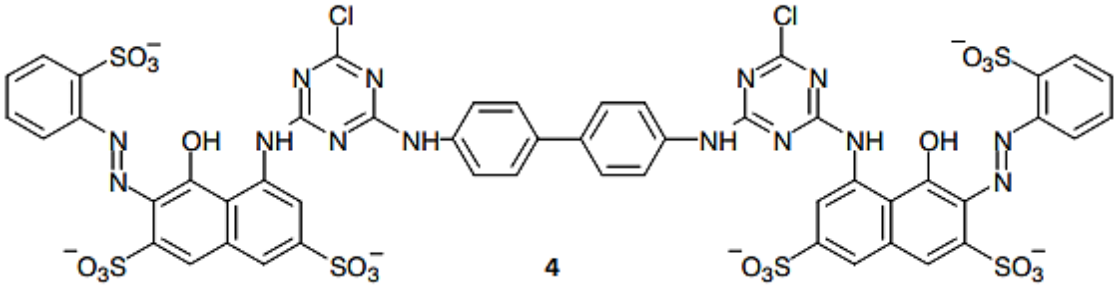

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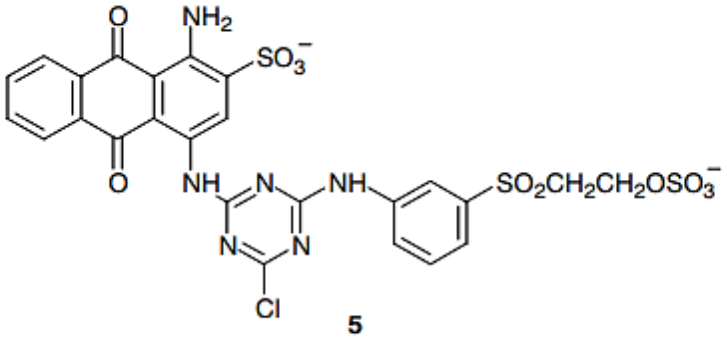


5

Functions of Reactive Dyeing Chemicals

1) Salt:

- ✓ To increase affinity of the dye to fibre.
- ✓ To decrease the hydrolyzed of the dye.
- ✓ To add extra energy to push the dye in the fibre.
- ✓ To neutralize the electro negativity of fibre.

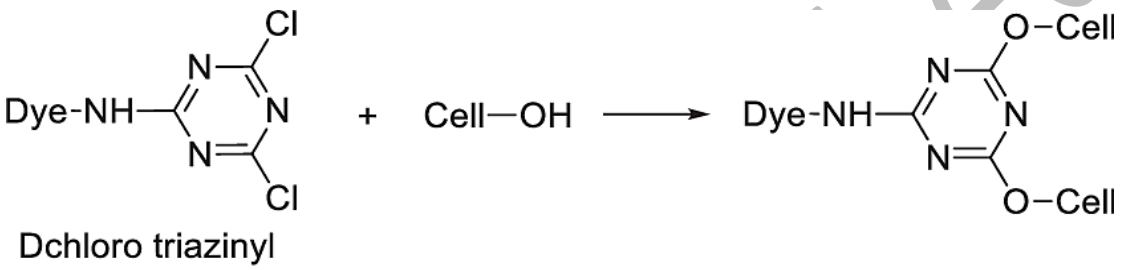
2) Alkali:

- ✓ To create optimum pH in the dye bath.

- ✓ It is used as a fixing agent.
- ✓ Without it no dyeing will take place.

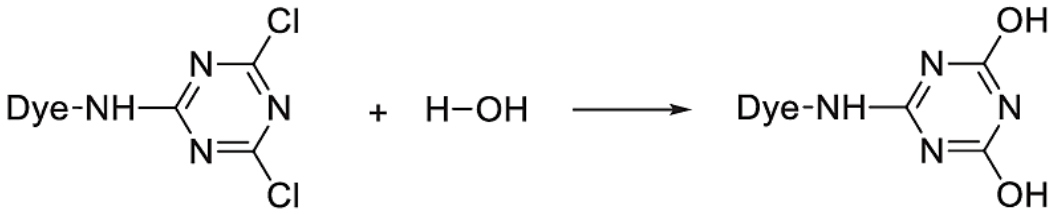
Hydrolysis of Reactive Dyes

- ✓ The reactive group of dyes may **react with water** as the increasing temperature which is simply referred as **hydrolysis**.
- ✓ **35-40%** dyes may go for **wastage** in this case.



Dchloro triazinyl

Fixation of dye with cellulose



Hydrolysis of dye with water

Factors Affecting Dye Hydrolysis

Liquor Ratio: M: L may be **1:5 – 1:10**. Higher liquor ratio **increases hydrolysis** and vice-versa

Concentration of electrolyte: Common salt and Glauber's salt. Concentration of salt may **be 20-100 g/L**. Depends on the **depth of shade (0.1-8.0**%). **Higher salt concentration decreases hydrolysis** up to a limit and vice-versa

pH: pH range for reactive dyes **10-12.5**. **Higher pH increases hydrolysis** and vice versa

Temperature: 40°C -100°C temperature is applied. Temperature of dyeing hydrolysis and vice-versa.

Dye reactivity: It increase both **hydrolysis and fixation** rate.

Time: The exhaustion takes in **20-30 min. Higher dyeing time increases hydrolysis** and vice –versa.

Type and no of reactive dye: vinyl sulphone is more prone to hydrolysis than **triazine group**.

Dye substantivity: More substantive dye causes more hydrolysis but if substantivity is reduce to bare minimum or removed altogether, the build-up problem arises during dyeing and color yield problem (dyeing) of the dye is reduced considerably.

Prevention of dye hydrolysis

- ✓ Application temperature should not be above $40^{O}C$.
- ✓ Relatively **large number of electrolytes** are required for the exhaustion, otherwise dye hydrolysis will occur greatly in dye bath.
- ✓ **Dye and alkali solution** should be prepared **separately and mixed** just before using.
- ✓ **Dye and alkali solution** should not keep for **long time after** mixing.

Reasons for Popularity of Reactive Dyes

- ✓ The reactive dyes show good washing fastness properly.
- ✓ The dyes have good light fastness property.
- ✓ Dyes are cheap in price.
- ✓ The dyes give brighter shades.
- ✓ The dyeing method is very simple.
- ✓ Less time and less temperature dyeing.

Stripping:

- ✓ To remove color from the fabric

Stripping of Reactive Dyes

- ✓ For **full stripping** the goods are first treated with **sodium hydrosulphite ($Na_2S_2O_4$) at boil**
- ✓ Then **washed off and bleached** with **1% sodium hypochlorite (NaOCl)** at **room temperature**.
- ✓ This is **carried out for 30 minutes**.

A typical recipe of stripping is given below :-

- **Na-hypochlorite (NaOCl)** : 1% at room temperature.
- **Na-hydrosulphite ($Na_2S_2O_4$)** : at boil temperature.
- Time : 30 minutes.