# LECTURE NOTE

**SUB: TEXTILE CHEMICAL PROCESSING - II**

**BRANCH: - TEXTILE ENGG.**

**SEMESTER: 4$^{TH}$**

# GOVERNMENT POLYTECHNIC, BHADRAK

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# SYLLABUS

## 1. Dyeing of Man made & their Blends

1.1 Discuss Dyes used for man-made fibres.

1.2 State Dyeing of polyester with disperse dyes by carrier ,HTHP and Thermosol method.

1.3 State Dyeing of Cationic dye-able polyester fibre

1.4 State the Dyeing of Polyester /Cotton and polyester /Wool blended fabrics with suitable dyes.

1.5 State the Dyeing of Acrylic with basic dyes.

## 2. Printing

2.1 State the objects of printing

2.2 Differentiate between dyeing and printing.

2.3 Preparation of printing paste & Classify and state the functions and properties of thickeners.

2.4 Methods & Styles of printing

2.5 Discuss styles of printing – Direct ,Discharge &Resist.

2.6 Discuss Different methods of printing –Block printing ,Screen Printing ,Rotary screen Printing, Roller printing ,Transfer printing .

2.7 Brief idea about preparation of screens for printing.

2.8 Printing of cotton fabric with suitable dyes like vat dyes, reactive etc.

2.9 State printing of wool ,silk & Nylon fabrics with acid dye & Polyester fabric with disperse dyes.

## 3. Mechanical finishing

3.1 State the objects of finishing & Classify finishes.

3.2 Discuss importance of mechanical finishes & State the objects of calendaring and working of different calendars.

3.3 State the objects of stentering & sanforization .

## 4. Chemical Finishing

4.1 State the objects of chemical finishing.

4.2 Discuss methods of application of Crease resistance finish, water proof and water repellant finish ,flame retardant finish , carbonization of wool ,Moth proof finish on wool, Stone wash on denim fabric.

4.3 Objects of Mercerisation , Physical, Chemical & Structural Changes occurred after mercerization of cotton fibre.

4.4 Factors affecting mercerisation., Discuss working method of chainless mercerisation of cotton fabric.

## 5. Washing & Drying

5.1 Importance of Washing.

5.2 Objects of drying.

5.3 Discuss Working principle of Hydroextractor , Multi cylinder drying, IR/ RF dryer.

# MODULE – I

# DYEING OF MAN-MADE FIBRE AND THEIR BLENDS

## 1.1 DYES USED FOR MAN MADE FIBRES

Dyes may be defined as the different types of colouring particles, differ each type from other type in chemical composition and are used for colouring fabrics, yarns in different fine of colors and shades and which are completely soluble in liquid substance. They are colored organic compounds that are used impart color to various substrates.
There are different types of dyes for **dyeing** textile goods. These dyes have different nature in fiber. It depends on fiber characteristics, chemical structure etc. The main classes of dyes most widely used for manmade fibre are as follows:

1. Acid dyes
2. Disperse dyes
3. Basic dyes

### 1. Acid dyes

***Non-metallised dyes***

These dyes can be applied to nylon, wool or silk in the pH range 3.0–7.0. The wet-fastness of these dyes varies from moderate to good and their light fastness is generally in the blue-scale range 5.0–6.0.

These small relative molecular mass (Mr) dyes are applied at low pH values so that dye–fibre substantivity arises from ion-ion electrostatic forces, for example, in nylon operating between the amino end group, which is protonated under acidic conditions and the anionic dye. Under these conditions the dyes display very good migration and levelling characteristics, but low wet-fastness. Dyes which have larger Mr exhibit higher substantivity for the fibre, but the migrational properties are lower although a higher wet fastness is achieved with these dyes.

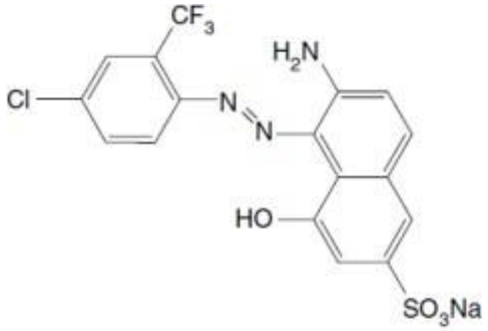
These dyes have been divided into three subgroups due to their varying application and fastness properties. Stevens 18 used a I–III grouping for classifying non-metallised acid dyes on nylon:

**Group I:**
Dyes with little affinity under neutral or weakly acidic conditions, but which exhaust under strong acid conditions

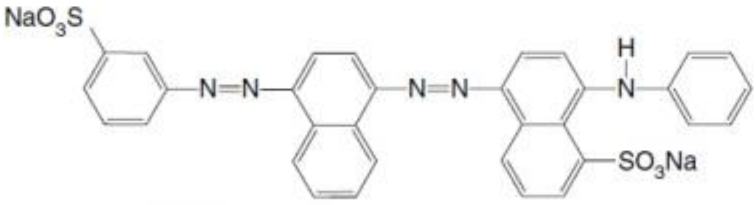
**Group II:**
The largest group of dyes that exhaust onto nylon within the pH range 3.0–5.0.

**Group III:**
Dyes that exhibit a high affinity for nylon under neutral or weakly acid conditions (pH 5.0–7.0).

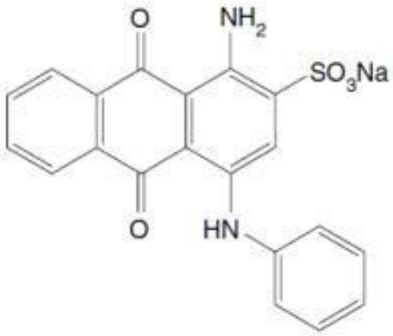
The water solubility of these dyes is due to the presence of one or more sulphonate groups (−SO 3 Na). These dyes belong to the azo chemical class which represents the largest class of dyes, providing an extremely large gamut of shades. Three examples of these dyes are shown in Figs.



C.I. Acid Red 266 (monoazo).



C.I. Acid Blue 113 (disazo).



C.I. Acid Blue 25 (anthraquinone).

There are several disadvantages associated with non-metallised dyes for some substrates: for example on nylon, low colour yield, lower wet-fastness properties and the tendency to barré dyeing. Also, due to the lower crystallinity of nylon 6 compared to that of nylon 6,6, dyes show a greater rate of uptake on nylon 6 for a given pH range.

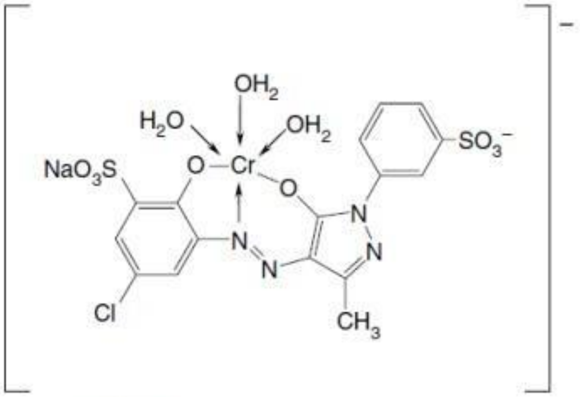
Non-metallised dyes vary in their ability to cover barré nylon. In general low Mr dyes exhibit better coverage than their higher Mr counterparts. Thus by careful dye selection it is possible to greatly minimise or even eliminate the effects of physical variations within the fibre. Eliminating chemical variations is more difficult to achieve.

The limited number of amine end groups (AEG) in the nylon fibre dictates the saturation value of the fibre by the non-metallised acid dyes. Once a dye anion has been attached to an amino group on the fibre, that group is 'neutralised' by the dye anion and so is unable to attract further dye anions.

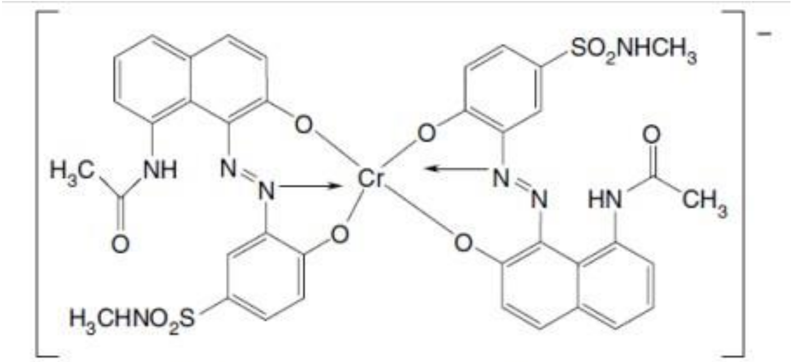
***Metal-complex dyes***

These dyes are based upon mordant dyes; the difference is that metal complex dyes have the mordant metal incorporated within the dye molecule so do not require a separate mordanting stage. There are two classes of metal-complex dyes – 1:1 metal-complex and 1:2 metal-complex dyes. As the names suggest, the metal-complex dye comprises one metal atom (usually chromium) coordinated with one or two molecules of a dye ligand. An example of each metal-complex structure is shown in Figs.

The 1:1 metal-complex dyes are applied under strongly acidic conditions for satisfactory migration to take place. These conditions can cause severe degradation of nylon fibres and this limits the use of these dyes for dyeing nylon. A few dye manufacturers have tried to overcome this problem by either using sulphamic acid in place of sulphuric acid or by the inclusion of a levelling agent to reduce fibre damage.



C.I. Acid Red 183 (1:1 metal-complex).



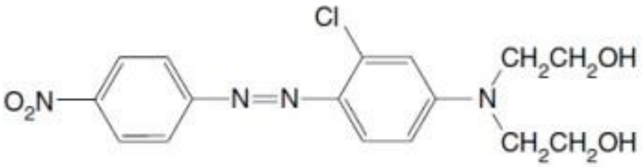
C.I. Acid Black 60 (1:2 metal-complex).

The 1:2 metal-complex dyes exhibit high saturation values and excellent compatibility in mixture shades and they have good light-fastness and . fastness properties. However, their ability to cover chemical variations within the fibre varies significantly and is dependent upon molecular size and substituent solubilising groups. The shade gamut of these dyes is restricted to dull shades and the class is deficient in bright blues and reds. There is a wide range of 1:2 metal-complex dyes available for nylon; different manufacturers' ranges differ in optimum pH range but they are generally applied from a neutral to weakly acidic dye bath.

## 2. Disperse dyes

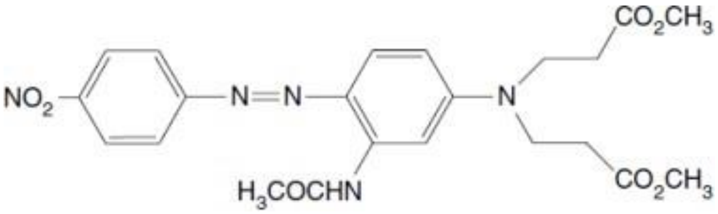
These dyes are frequently insoluble or sparingly soluble in water, non-ionic in character and applied to hydrophobic fibres from an aqueous dispersion. They are predominantly used on polyester but have found application to nylon, cellulose acetate and acrylic fibres, although some of the wet-fastness properties of the dyes on these substrates are poor. The dyed substrate is usually given a reduction clear following dyeing, in order to clean the substrate surface of dye that would cause staining if left untreated.

These dyes were traditionally applied to polyester at the boil with the inclusion of a carrier in the dye bath to facilitate diffusion of the dye into the substrate. Carriers caused many problems to the dyer including residual smell of carrier on fabrics and reduced light-fastness of dyed fabrics due to residual carrier. Since the advent of pressurised dyeing machines, these dyes are now applied to polyester without carriers at temperatures around 130°C; the reduction clear is still conducted after dyeing. A typical disperse dye structure is shown in Fig.



Chemical structure of a disperse dye (C.I. Disperse Red 7).

The ***reduction clear*** is an extra cleaning step which increases processing time and cost together with adding to the effluent load from the dyeing process. There have been attempts to create dyes that become water-soluble in mildly alkaline conditions in order to eliminate the reduction clear process. The Dispersol C dyes from DyStar are one such brand. These dyes had either a sulphonyl fluoride Or, more commonly, a number of carboxylate ester groups on the molecular structure of the dye. During alkaline scouring after dyeing these groups are converted to their water-soluble sulphonic/carboxylic acid forms rendering the dyes water-soluble, therefore dye which was still on the surface of the substrate would be dissolved in the wash-off liquor and the result would be a clean surface of the substrate. An example of the Dispersol C dyes is shown in Figure.



Chemical Structure of an alkali-clearable disperse dye (C.I. Disperse Red 278)

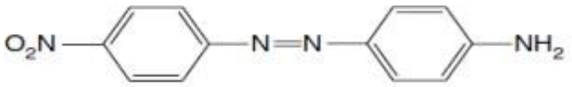
Disperse dyes have also been used in thermal transfer printing. This can be conducted using several methods.

***Pad thermofix***

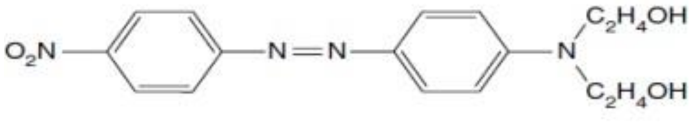
The fabric is padded with dye dispersion and following drying, subjected to a high temperature for a short duration (typically 30–60 s) whereby the dye diffuses into the substrate. The selection of dyes able to undergo sublimation is critical for this process; this rules out the use of the 'high energy' type Of disperse dyes.

***Paper transfer printing***

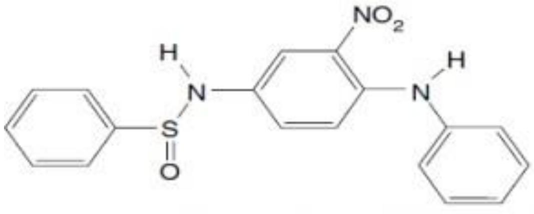
The design required is printed in reverse on a transfer paper. The paper is placed firmly against the substrate which passes between two pressurized heated rollers. The design on the paper is transferred to the substrate via sublimation of the dyes.



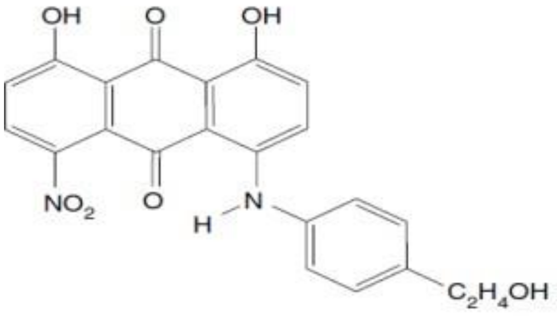
Class A disperse dye (C.I. Disperse Orange 3).



Class B disperse dye (C.I. Disperse Red 19).



Class C disperse dye (C.I. Disperse Yellow 42).

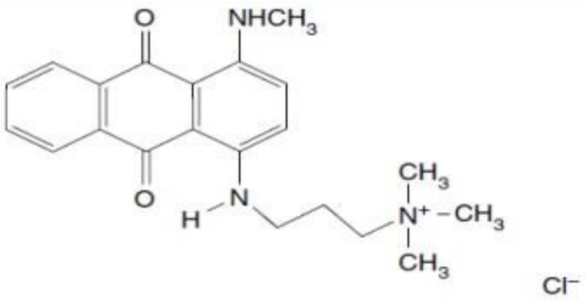


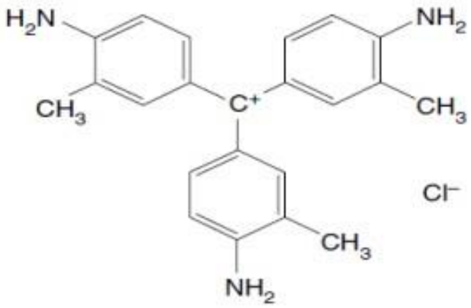
Class D disperse dye (C.I. Disperse Blue 27).

Disperse dyes are classified by their sublimation temperature: Class A dyes have the lowest sublimation temperature whilst Class D dyes have the highest sublimation temperature. The sublimation temperature is also relative to the molecular size of the dyes. Class A dyes are relatively small in molecular size whilst Class D dyes are significantly larger than Class A dyes. Examples of disperse dyes from Class A to Class D dye are shown in Figs.

**3. Basic dyes**

These dyes are usually applied to acrylic, paper and nylon substrates, but can also find use in some modified polyester substrates. Basic dyes are


Localised charge basic dye (C.I. Basic Blue 22).


Delocalised charge basic dye (C.I. Basic Violet 2).

Water-soluble and produce coloured cations in solution; these cations are attracted electrostatically to substrates with a negative charge. Basic or cationic dyes can have either the positive charge localised on an ammonium group (these dyes are characterised by a high tinctorial strength), or it can be distributed as a delocalised charge over the dye cation as found in many triarylmethane, xanthenes and acridine dyes. Examples of a localised and a delocalised charge dye are given in Figs. 1.26 and 1.27, respectively.

Basic dyes are often applied with retarders due to their poor migration properties at the boil. This poor migration is due to the high substantivity of the dye for the substrate and rapid increase in diffusion at high temperatures. Careful control is necessary when using retarders so that anionic sites within the substrate are not blocked which would restrict dye uptake making it difficult to achieve dark shades.

## 1.2 DYEING OF POLYESTER WITH DISPERSE DYES

### a. Brief description of structural parameter of polyester making it difficult to dye.

**Introduction** – Of all the manmade fibers polyester fiber is known in the trade as Terene, Dacron etc. is the most widely used synthetic fiber and its blend with cotton and wool almost popular for dress material.

Chemically polyester is a polymer of an ester obtained by condensing Terephthalic acid with ethylene glycol. Both the raw material is obtained from petroleum products.

**Structural parameter of polyester making it difficult to dye** – Polyester present more difficulties for dyeing at normal dyeing conditions because the polymer chains in polyester are much more closely packed than those in cellulose acetate. The dye stuff particles of dye therefore, don't easily penetrate the fibers and in fact, the process of diffusion of dye is so slow that it takes Week to dye polyester fiber at a temperature of 85ºC.

The dyeing of hydrophilic fibers like cotton and wool is not as difficult as the dyeing of hydrophobic fibers like polyester. The hydrophilic fiber swell on wetting with water and the dye solution taken up by them, occupies the amorphous region in the fiber molecule .And by increasing the temperature the dye molecule diffuse faster in to fiber structure.
In case of hydrophobic fiber water does not swell the fiber because of the following parameters –

1. **High degree of orientation** – The polyester fiber having high degree orientation because of that the dye molecule are not able to diffuse inside the structure of polyester fiber at normal dyeing condition .
2. **High cohesive forces**- The macromolecule of polyester are connected to each other by strong cohesive forces. That's why it is difficult to dye at normal dyeing condition. Dye molecule unable to diffuse between them because of high cohesive force.
3. **Compact structure** –The fiber structure is so compact because of that water is not able to swell the fiber and result negligible amount of water is imbibed in the fiber structure .in sort no space between micro molecules.

**b. Need principle and method of heat setting of polyester.**

The stabilisation of dimensions of synthetic fabric is by exposure to heat is possible because of one peculiar property of these fibers namely, that the fiber resist shrinkages at high temperature (below melting point) if they are held at these temperature for a short period of time thus it become dimensionally stable. This operation is crucial for fabrics made of synthetic fibers, for triacetate, and partly for PAC fibers, since it grants excellent dimensional stabilisation and crease proof properties, maintained till the fabric is exposed (by air blowing) to temperatures exceeding the heat setting one. After being treated with water at a temperature above the second order glass transition temperature i.e. 80-85°C for acrylics.

**Need of heat setting –**Heat-setting is a heat treatment by which shape retention, crease resistance, resilience and elasticity are imparted to the fibers. It also brings changes in strength, stretchability, softness, dye ability and sometimes on the colour of the material. All these changes are connected with the structural and chemical modifications occurring in the fiber.

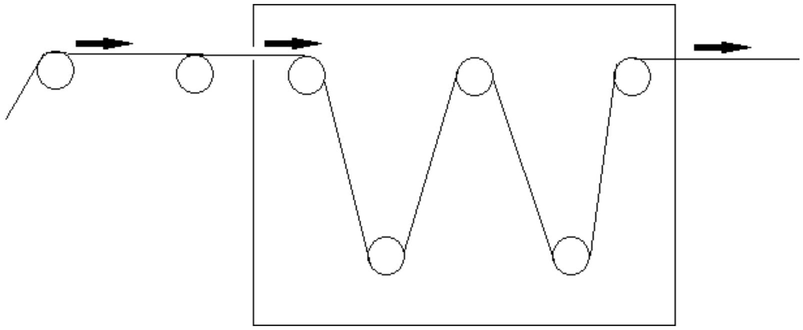
**Stages of Heat Setting-** Heat-setting can be carried out at three different stages in a processing sequence i.e. in grey condition; after scouring; and after dyeing. The stage of heat-setting depends on extent of contaminations and types of fibers or yams present in the fabric. Heat setting after dyeing could lead to the sublimation of disperse dyes (if not accurately selected).Heat setting is carried out on gray fabrics, on scoured fabrics (frequently applied) and on dyed fabrics (scarcely applied). The process grants excellent dimensional stability and good crease-proof properties. As far as operating conditions are concerned, the fabric must be treated in accurately controlled moisture and temperature conditions. Polyester fabrics can be dimensionally stabilised by heat setting at a specific temperature so that they don't undergo any change in dimension in subsequent processing such as washing or dry cleaning .heat setting consist essentially of exposing the fabric while under dimensional control to a temperature 30°C to 40°C above the temperature likely to be encountered in its subsequently processing or use. Accordingly for fabrics which are intended for apparel wear and which may be ironed a temperature of 220°C to 230°C is suitable setting temperature. This process make the fabric stiff but this stiffening is removed in subsequent processing sometime the fabric is even heat set before scouring so that the stiffness of the fabric disappears in processing .if the fabric is not heat set very troublesome creases appears on washing which are difficult to remove.

**Method s of Heat setting –**

- **By Stenter machine.**
- **By curing chamber.**

(Mostly dry heat or radiant heat is preferred for heat setting sometimes steam is also used)

**Stenter Machine-**Stenters is widely used for stretching, drying, heat-setting and finishing of Fabrics. The stenter frame is usually 80-100 feet long and 70-100 inches wide. The speed ranges from 10-45 m/min with a maximum setting time in the setting zone 30 sec at temperature ranging from 175 to 250°C depending upon the thickness and type of the material.



Chamber where temperature is maintained as per requirement (175-250$^{o}$C) and speed ranging from 10 - 40 meters per minute. Mostly for heat setting dry air is preferred but some time steam is also preferred in but this method is undesirable as it causes some hydrolysis of the ester groups in the polymer chain due to that material loss its strength.

Stenter machine in heat setting

## Approaches for dyeing, various methods of dyeing polyester involving use of chemical and thermal energy (careers dyeing and, HTHP)

### Approaches for dyeing-

The difficulties, in dyeing were overcome by Ellis who invented the S.H.A. colors' which are applied from an aqueous dispersion (and not from a solution) which has greater affinity for the fiber than the water in the dye bath. Thus the disperse dye migrates from the liquor and dissolves in the fiber. This method is called disperse dyeing and has been used on almost every new fiber that has been developed. Polyester presents more difficulties than other fiber because the polymer chains in polyester are much more closely packed than those in cellulose acetate. The dyestuff particles of disperse dye, therefore, do not easily penetrate the fibers and in fact, the process of diffusion of the dye is so slow that it takes weeks to dye polyester fiber at a temperature of 85°C. The dyeing of hydrophilic fibers like cotton and wool is not as difficult as the dyeing of hydrophobic fibers like Polyester. The hydrophilic fibers swell on wetting with water and the dye solution taken up by them occupies the amorphous region in the fiber molecules and by increasing the temperature the dye molecules diffuse faster into the fiber structure. In the case of hydrophobic fibers, water does not swell the fibers because of their compact structure and when the fiber is entered into the dye bath practically no water enters the fiber structure; the dye molecules do not diffuse into the fiber and the dyeing is, therefore, difficult. This difficulty in dyeing has been overcome by adopting four different methods as under:

**By suitable dye –** by using selected disperse dyes have very small molecular size which can readily diffuse in to fiber structure.

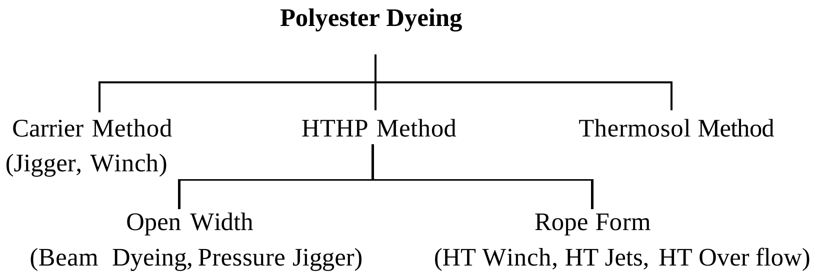
**By opening of fiber structure –**there are two different methods are available for loosen up the fiber structure or opening up of fiber structure

- **By Temperature**- the molecular structure of polyester opened up at high temperature means the bonds get weak and dye molecule get diffuse in to the internal structure of polyester. (180-230$^{o}$C depends on material quality and manufacturing specifications).
- **By chemical (carriers or swelling agent) –** By the help of chemicals like carriers the structure of polyester are also opened at lower temperature. The swelling action of carriers causes diffusion of due molecule easily in to the fiber structure.

**By modification of dyeing technique –** by modifying the technique of dyeing to bring about easy diffusion of the dye molecule directly in to fiber by a process known as thermosol Dyeing Technique. Now a day's mostly HTHP machines are preferred for dyeing of polyester.

## Various methods of dyeing of polyester –

## Polyester Dyeing



### 1. Carrier Method:

Certain chemicals called carriers are added to the dye bath; they are in fact the swelling agents for the fibers. They swell the fiber at boil enabling the chain molecules to move about more easily and increase the distance between them so that there is more space to accommodate the dyestuff molecules. The swollen fibres permit large dye molecules to diffuse more rapidly in the fiber. Thus the carriers increase the solubility of the dye and the rate of dyeing and are absorbed by the fiber. Some of the chemicals used as carriers are; O-phenyl phenol, P- phenyl phenol, dichlorobenzene (Tumescol BDN of lCl), trichlorobenzene (Dilatin TC of Sandoz), dimethyl terephthalate etc. The carriers enable dyeing to be carried out at boiling temperature without the use of special equipment such as high pressure vessels which are expensive.

The carrier is usually added first or is added slowly during the dyeing process because if it is added at once, the dyestuff may rush on to the material.

### (a) Method of dyeing Using Tumescol OP (0-phenyl phenol) as Carrier:

The dyebath is set with 1 gm/l Lissapol D, 0.75 gm/l Dispersol AC, and 3 to 5 gm/l Tumescol OP at 40°-60°C. The material is worked in the blank bath for 15 minutes taking care to see that the carrier gets uniformly absorbed. The well dispersed dye is then added and the temperature raised to boil within 30 minutes. The pH of the bath is maintained 6.5 to 7 by adding 1 ml/l acetic acid for liberation of phenol. The dyeing is continued at boil for 2 hours.

The material after dyeing, is rinsed and soaped at boil with 2 gm/I Lissapol D and 2 to 5 ml/l caustic soda (72°Tw) at 80$^o$ -85$^o$C for half an hour to remove residual carrier, this is important as its presence impairs the fastness to light of the dyed material and it causes irritation of the skin and gives unpleasant odour. The last traces of the carrier can be completely removed by curing at 190$^o$C to 200$^o$C for one minute when it sublimes.

### (b) Method of Dyeing with Dilatin B or Dilatin C as carrier:

Dichlorobenzene marketed as Tumescol BDN (by ICI) and as Dilatin B (by Sandoz) and trichlorobenzene marketed as Dilatin C (by Sandoz) can be used for dyeing as under: The dyebath is set with 1 gm/l Ultravon W and the goods are run for a short time at 50°C. 3 to 5 ml/l carrier and 1 ml/l acetic acid (40%) are then added and the goods run in the blank bath for 15 minutes; the dye is then added at 60° to 70°C and the temperature of the bath is raised to boiling point within 30 minutes and dyeing continued at boil for 2 hours. The goods are then rinsed, treated with 1 gm/I Ultravon W at boil and washed.

**The carrier dyeing method has certain advantages as well as disadvantages. The advantages of carrier dyeing method are that:**

- The material can be dyed at atmospheric pressure without using any special equipment.
- The carrier helps the dyestuff in penetrating the fibre.
- The dyeing can be carried out comparatively rapidly and
- The dyeing is more or less uniform.

**The disadvantages of Carrier dyeing method are:**

- The carriers are costly; the cost of dyeing is, therefore, considerable.
- The goods retain the odour of some of the carriers if not washed thoroughly.
- The light fastness of the dyeing is badly affected.
- It is difficult to remove the carrier completely from the dyed material; residual carrier can cause irritation of the skin.
- The process of dyeing is rather lengthy.

**Reduction Clearing**: When the dyeing is not carried out properly or when dyeing a heavy depth of shade, loose dye may get deposited on the fibre after dyeing. This deposition leads to poor fastness to rubbing; hence it has to be removed. This is done after dyeing and before soaping by what is known as the reduction clearing treatment.

The dyed material is treated in a bath containing:

2 to 3 gm/l Lissolamine A (or Dispersol .VL) 6 ml/l caustic soda (68°Tw) and
2 gm/l sodium hydrosulphite at 50°C for 30 minutes and rinsed.
If the material is dyed at a temperature above 100°C it is treated in a bath containing

5 gm/l Dispersol VL (or 3 gm/l Lissolamine RC) 3 gm/l caustic soda flakes and
2 gm/l sodium hydrosulphite at 85°C for 30 minutes, soaped, washed and dried.
The above treatment removes the dyestuff which lies on the surface of the fibre but does not remove that which has penetrated into the fibre.

## 2. High Pressure High Temperature (HTHP) Dyeing

The disperse dye stuffs without the use of carriers do not penetrate (or partly penetrate) the polyester fiber even at 100°C and give only pale shades as most of the dye stuff is located on the surface of the fibers. If however, the temperature is raised beyond 100°C say, to 120°C, the chain molecules in the fibre are much freer to move and the fibre swells to a greater extent. As a result there is rapid penetration of the dyestuff molecules in the fibre structure. The dyeing time is also reduced due to faster diffusion of the dye in the fibre. The fastness properties of the dyed material are improved due to better penetration of the dye and the disadvantages of carrier dyeing are eliminated. The process, however, involves the use of pressure equipment since water dye baths cannot be maintained at a temperature above 100°C at atmospheric pressure. The dyeing has therefore, to be carried out at high pressure and high temperature in closed vessels.

**Method of Dyeing:** The method of dyeing is quite simple. The dyebath is set with 1 gm/I dispersing agent and made acidic with 1 ml/I acetic acid (40%) to bring the pH of the liquor 5.5 to 6. If the dyebath is alkaline, loss of strength of the fibre occurs at high temperature. The goods are entered at 60°C in the pressure vessel and the temperature raised to 130°C quickly. The dyeing is carried out at this temperature for 30 minutes for pale shades and for 1 hour for dark shades. The liquor is then run off and the material is rinsed. If it has been dyed a heavy shade it is given a reduction clearing treatment and it is then soaped with 1gm/l Lissapol D at 80°C for 30 minutes, rinsed again and dried.

## 3. Thermosol Method of Dyeing

This process was developed by du Pont in 1949 for dyeing polyester with disperse dyes without using carriers. The principle of this method is that polyester fibres which are thermoplastic soften when heated to high temperature and many disperse dyes at that temperature melt with the result that the molten dye dissolves in the fibre which itself is in a plasticized or viscous state. In the actual process, the dye is applied by padding from an aqueous medium; the fabric is dried to remove water thereby leaving the dye on the surface of the fabric. After drying, the fabric is exposed to a high temperature (205°C) for a minute during which the dye "dissolves" in the fibre and becomes so fast that it cannot be removed even by most severe laundering. Any unfixed dye is then removed by reduction clearing. Yarn in the form of skeins or hanks can also be dyed by this method by using a simple yarn padder. The hank is padded with a fine dispersion of the dye, squeezed, dried, stretched and then cured at 205°C for a minute.

The fabric is heat-set before dyeing. It is then padded on a three bowl padding mangle with two dips and two nips. The padding liquor contains 3 to 4% CMC or 2 gm/l sodium alginate thickener (1:4) to ensure even dyeing and prevents dye migration; the pH of the bath is adjusted between 6.5 and 7 with 12 gm/l mono sodium di- hydrogen phosphate ($NaH_2PO_4$).

A volatile solvent like butanol is also added to the padding liquor to assist uniform spreading of the dye on the fabric surface. The padded fabric with 60% pick-up is then carefully dried. Uniform drying is the most important step in this method. Slow and even drying is essential.

In the conventional drying equipment, the moisture is removed from the surface of the fabric as vapour as a result of which more water is drawn to the surface from the interior of the fibres; due to this internal movement of water migration of dye takes place. There is also a difference in the rate of drying between the two sides of the fabric which leads to two-sided effect. Infra-red drying which eliminates dye migration is the most suitable method. Due to radiant heat, water is evaporated not only from the fabric surface but also from within the fibres and the drying is uniform. The moisture content of the fabric is reduced from 60% to 30% by radiant heat. The fabric is then further dried on a range of 14 steam-heated cylinders the first 4 of which are coated with Teflon to prevent sticking. The fabric is then cured in a curing oven or stenter or in hot roll equipment at 205°C for 1 minute, whereby 75 to 90 % of the dye is fixed. During heating the fabric has to be kept free from wrinkling and both the sides of it have to be heated uniformly.

The Thermosol range consists essentially of a padder, an infra-red drying unit, a cylinder drying range, a hot flue thermosol oven, a steaming unit, an open soaper and washing tanks.

This process can be applied to polyester-cotton blended fabrics also. The polyester component is first dyed on the thermosol range with disperse dyes and then the cotton component is dyed with suitable dyes on a pad-steam range.

**Advantages of this process are:**

- No carrier is requires in dyeing; hence the high cost of carrier and its adverse effect on light fastness of the dyed material are eliminated.
- It is a continuous process; therefore, large quantities of the material can be dyed more economically than by the batch process.
- Most of the dye i.e. 75 to 90 % is fully utilized in dyeing;

## 1.3 DYEING OF CATIONIC DYE-ABLE POLYESTER FIBRE

Cationic Dyeable Polyester is a special Polyester fiber which has undergone a change during polymerization. They were built of molecules of 5 - sulphophthalic acid, to generate anionic sites that the fibers of normal PET not have. Having anionic groups it can also be dyed with cationic dyes with results of high brilliance. However, these fibers can be dyed with disperse dyes. Compared to ionic dyes, disperse dyes have smaller molecular extinction coefficients and lower build-up property, so these dyes cannot give bright and deep colors. This type of fibers were born also to lower the Tg (glass transition temperature) of the polymer, 10 ° C lower than normal Polyester fibers, so to obtain a more segmental mobility and open polymer structure. Resulting in increased rate of diffusion of the dye in the fiber at a lower temperature. Tg Range (70 – 85°C). This modified polymer is also more easily hydrolised and more sensitive to heat setting before dyeing at a maximum temperature of 180°C.

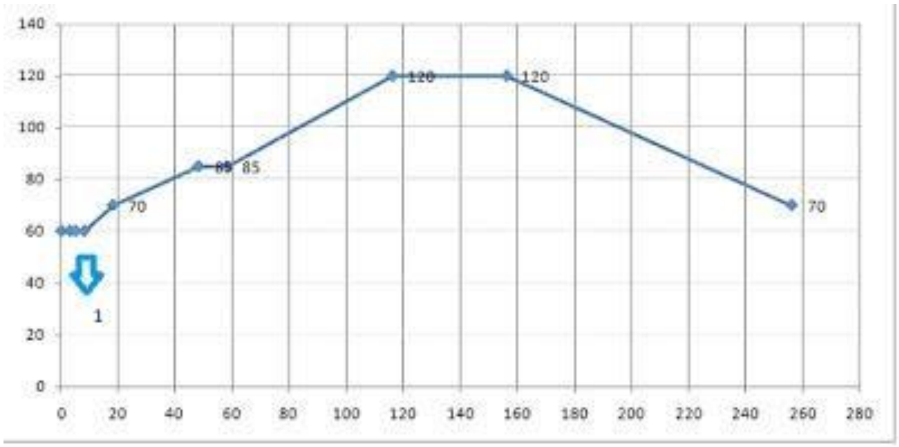
**Example**

Scouring and dyeing exhausted process in Overflow – Jet Machine (Liquor ratio - 1:10 – 1:20) :
Scouring:
Continuous washing cold for 10 min
Drain well (for water soluble oils)

Fill with water 30 ° - 35°C
0,5 g/l Antifoam (preferably non-silicone) alone
1 g/l Detergent non – ionic
0,5 g/l Caustic Soda 36° Bè
Raise to 80°C quickly and hold for 20 – 25 min
Drain well
washing cold for 10 min and after starting in dyeing.

**Dyeing with Cationic dyes**

Follow the Graph below :



The dye bath is set at 60°C - introduce order
0,5 g/l Antifoam (alone)
6 g/l Sodium sulphate (only dyeing at 120°C) (1)
1 g/l Dispersant non-ionic
X g/l Acetic Acid pH = 4,5

X % Levelling – Carrier anionic (only dyeing at 98°C)
X% Cationic dyes (dissolved at 60°C with 1 g / l of acetic acid) - (introduce preferably dosed curve progressive Sen +)

Then raise to 70°C - after to 85°C at 0,5°C / min (while the fiber is softening) and hold for 10 min, after raise to 120° (or 98°C) at 0,6°C / min – hold for 30 – 60 min (depends on the depth of the color)
then cool to 70°C at 0,5°C / min and check the color.

Please note that sodium sulphate (Na +), being very stable at high temperatures, is the protector of te anionic sites sensitive to the acid at 120 °C.

After dyeing, the dyed samples were rinsed and washed with 2 g/l of non-ionic detergent at 60 – 70°C.
**Light fastness:** moderate to good
**Wash fastness:** good to excellent
**Rubbing fastness:** good
Excellent resistance to **sublimation** on wet
No fouling of lycra mixed

## 1.4 DYEING OF POLYESTER /COTTON AND POLYESTER /WOOL BLENDED FABRICS WITH SUITABLE DYES.

### DYEING POLYESTER /COTTON BLENDS

### Introduction

There is a major market for 65/35 and 50/50 polyester/cotton fabrics for a varietyof end-uses, in weights ranging from light shirting to heavy industrial fabric. A variety of different batch and continuous dyeing processes are used for these. The dyeing of blends of polyester with other cellulosic fibres such as viscose and linen follows much the same principles outlined here, although there are some slight differences in the actual details.

The dyeing properties of polyester and cotton fibres are quite different and most of the dyeing methods for their unions involve separate steps for the colouring of the two fibres. The polyester component is invariably dyed first with a mixture of disperse dyes. For the cotton, there is a choice of dyes, the actual selection depending on the desired colour, the type of finishing required, the demanded fastness properties, the costs and the type of machinery available. The cotton is usually dyed with reactive, direct, sulphur, vat, or azoic dyes. The use of the latter three types is decreasing because of increased costs and environmental problems.

The reactive/disperse dye combination for dyeing cotton/polyester clothing fabrics is very popular. If the cotton is dyed first, subsequent pressure dyeing of the polyester at 120–130 °C can change the shade of the dyed cotton because the cotton dyes are less stable at high temperatures. Dyeing the polyester before the cotton allows an intermediate reduction clearing of any disperse dye on the polyester surface or remaining in the cotton (Section 15.7.4). An alkaline solution of hydros destroys several types of cotton dyes so that reduction clearing is precluded after dyeing the cotton. In addition, once the polyester is dyed any detrimental effects of required cotton dyeing assistants such as alkali and salt on the disperse dyes are avoided.

Cross-staining of the cotton by disperse dyes can be a problem. The stained cotton has poor light and washing fastness and the weakly held disperse dyes will transfer colour to other synthetic fibres such as nylon during washing. For deep shades, alkaline scouring, or preferably reduction clearing with alkaline hydros and a non-ionic detergent, removes the disperse dyes staining the cotton. Because cotton crosslinking agents used in the finishing of cotton/polyester fabrics require the use of relatively high curing temperatures, the disperse dyes used for the polyester must be of the types that have higher sublimation fastness. Therefore, high-energy disperse dyes are preferred. For fabrics with more than 60% polyester, the cotton component may not even be dyed if the required shade is only pale and the two fibres are well blended in the yarn.

As always, careful fabric preparation is essential for production of high quality dyeings. The aim is to produce a fabric that is easily wetted and absorbs dyes as uniformly as possible. It is imperative that singeing does not produce small masses of melted polyester on the fibre ends since these tend to dye more deeply than the fibres resulting in a fabric with a spotty appearance. Heat setting the polyester before dyeing, to stabilise the fabric dimensions, must be uniform since it influences both the rate and extent of dyeing with disperse dyes. Heat setting after dyeing helps to remove creases in the fabric and to set its final dimensions. It can, however, cause thermal migration of the disperse dyes in the polyester fibres. In the case of poorly penetrated fibres, disperse dyes may migrate further into the polyester fibre interior, thus deepening the shade. Alternatively, if any hydrophobic chemical such as non-ionic surfactant or fabric softener remains on the polyester fibre surfaces, disperse dyes may migrate into this layer, in which they are very soluble. This results in greater ease of colour removal by washing or rubbing during use, and is undesirable.

In many cases of union dyeing, the dyes and dyeing conditions for colouring one of the fibres influence the other fibre and its dyes. The major areas of concern are:

(1) the degree of cross-staining. Although disperse dyes will stain cotton, the anionic cotton dyes usually completely reserve the polyester. The disperse dyes selected should be those that give minimal cotton staining;

(2) interactions between dyes and auxiliaries when present in the same bath. For example, many disperse dyes are not stable under the alkaline reducing conditions used in leuco vat dyeing. The salt and alkali required for dyeing cotton with reactive dyes often have a deleterious effect on the dispersing agent for disperse dyes and cause particle aggregation;

(3) the conditions for fixation or aftertreatment of one type of dye on the other types often limits the processing methods that are possible. Thus, if direct dyes are used for continuous dyeing in combination with disperse dyes they must be stable to the high temperatures used in the Thermosol process. This factor influences when reduction clearing can be used. It is not possible to clear disperse dyes staining the cotton with an alkaline hydros solution if the cotton is already dyed. All the types of dyes used to colour cotton will be reduced under these conditions and the colour destroyed.

Even when staple polyester is the predominant fibre in intimate blends with cotton, the cotton fibres have a tendency to migrate to the yarn surfaces and have higher visibility. The colour and the fastness properties of the dyed cotton are therefore important, even though it is the minor component.

One of the major problems in dyeing cotton/polyester fabrics is that of colour control. This is true for cross-dyeings and for solid shades. To examine the colours of the individual fibres after dyeing, they must be separated. This is not easy. For simple evaluation of dyeing, small swatches of 100% polyester and 100% cotton fabrics, with characteristics close to those of the fibres in the blend, can be sewn onto the cotton/polyester material and their colours examined after dyeing. This avoids having to separate the two kinds of fibres. Alternatively, a widely used technique is to evaluate the colour of the dyed blend and then to dissolve out the cotton with 70% aqueous sulphuric acid. The polyester is unaffected by this and a polyester ‘skeleton’ remains, the colour of which can be examined. The colour of the cotton is assessed from the difference between the colours of the original fabric and the residual polyester skeleton.

Because a mixture of dyes is needed for dyeing this type of fibre blend, and because there are a number of potential problems, consultation with a dye manufacturer is recommended in selecting dyes and processes. Suppliers are able to recommend disperse dyes that minimise staining of the cotton, suitable dyes for the cotton, and point out inappropriate dye combinations.

## DYEING POLYESTER /WOOL BLENDS

Fabrics containing a blend of polyester and wool have superior abrasion and crease resistance to those made from wool alone, yet they retain the valued warmth and handle of wool fabrics. In many cases, where the highest quality and good fastness properties are essential, the two fibres may be dyed separately before blending and fabric construction.

The dyeing of wool/polyester mixtures, using acid dyes for the wool and disperse dyes for the polyester, allows the production of solid shades and all types of cross dyeing. In the two-bath dyeing process, the polyester is first dyed with the disperse dyes under pressure at up to 130 °C using a weakly acid dye bath at around pH 5. Dyeing times should be short since the wool is more prone to damage at temperatures above 105 °C. In dyeing wool/polyester unions, the disperse dyes may stain the wool fibres in the blend and the long time required for their migration to the polyester can cause a loss of wool quality. Any residual disperse dyes in the wool must be removed under the mildest conditions possible by soaping with a non-ionic detergent solution at 70 °C. Alternatively, reduction clearing with a weakly alkaline ammonia

solution of hydros or formaldehydesulphoxylate avoids damaging the wool. Acid dyes then dye the wool under weakly acidic conditions in a second bath.

In the one-bath process, fast acid and disperse dyes are applied simultaneously from a weakly acidic dyebath, followed by soaping. In deep shades, staining of the wool by disperse dyes is heavy and unless the soaping treatment is effective, the washing fastness of the dyeings may be inferior. The one-bath dyeing method is useful mainly for pale to medium depths of moderate fastness. Both the acid and disperse dyes are applied simultaneously using a polyester dyeing carrier at the boil at pH 4–5. The use of a carrier avoids the lengthy times for the transfer of disperse dye held by the wool to the polyester. The wool must be cleared of disperse dye by scouring with non-ionic detergent. Reduction clearing is not possible in this case, since the wool is already dyed with dyes sensitive to reducing agents. Alternatively, a one-bath process at 120 °C uses a wool protection agent and there is little cross-staining of the wool by the disperse dye.

## 1.5 DYEING OF ACRYLIC WITH BASIC DYES

### Structure aspect of acrylic affecting their dyeing behavior

Introduction: Acrylic fibres which were introduced in 1950 occupy an important place in the synthetic fibre industry. These fibres appeared in our country under the name "Cashmilon" they are marketed under various trade names such as Orion, Creslan, Drelan, Courteiie, and Acrilan etc. When the acrylic polymer was first made it could not be transformed into commercially useful product because suitable organic solvents which could be used for preparing solutions of polyacrylonitrile were not known. The solvents which are normally used such as acetone, ethyl alcohol etc., were of no use. The acrylic fibre became a commercial reality with the discovery in du Pont laboratories of suitable organic solvents for preparing solutions of polyacrylonitrile. A number of solvents have been patented; among these are: dimethoxy acetamide, dimethyi acetamide, dimethyi formamide and the Meta and Para nitro phenols.

Acrylic fibre is prepared by the polymerization by heat or peroxide of acrylonitrile $CH_2 = CH\text{-}CN$ another name for which is vinyl cyanide. Aciylonitrile is a fairly volatile liquid obtained from ethylene oxide with hydrocyanic acid.

According to the modern process known as the Sohio process, acrylonitrile is made from propylene and not from ethylene oxide because this process is economical. The acrylonitrile monomer alone or together with another monomer selected for co-polymerization is polymerised in the presence of a suitable catalyst at appropriate temperature and time. The polymer is then blended and dissolved in a suitable solvent. The solution is then filtered. The fibre is spun by the wet or dry process. The solution of the polymer is forced through a spinneret into a medium where solvent is removed and the solid filaments are formed. Acrylic fibre possesses a very pleasing, warm and soft handle; fabrics made from it exhibit a silk like luster, hand and drape.

Dyeing Behavior: A 100 % acrylic fiber is very difficult to dye because of its compact structure. This is mainly due to the high glass transition temperature (tg) of the fibre viz. 105°C; this means that the fibres become thermoplastic at or above this temperature. Below this temperature the fibres form a barrier to the approaching dye molecules. However, above the glass transition temperature, the fibre molecules change to a thermoplastic state so that when they come in contact with a dye molecule at this temperature the dye molecules are able to penetrate into the fibre. Fibres made from cent per cent acrylonitrile are not, therefore, used commercially. 85 to 90% of acrylonitrile is co-polymerised with 10 to 15 per cent of a monomer to make the fibre readily dyeable. The commonly used co-monomers in acrylic fibres are vinyl acetate, methyl methacrylate. The addition of co monomers decreases the glass transition temperature of the fiber (from 105°C) and thus increases the diffusion rate of the dyestuff. Most modern acrylic fibres have a tg of about 70° -80°. These fibers are two types

- Those containing acidic groups such as Orion 42 which can be dyed with basic dyes and
- Those containing basic groups such as Acrilan which can be dyed with acid dyes.

The Orlon-type acrylic fibres are more important than Acrilan-type fibres as the former are most widely used. The presence of the co-monomers in the fibres modifies their thermoplastic properties and dyeing properties are improved so that disperse dyes and basic dyes can be applied below 100°C in conventional equipment. Another important factor that affects the dyeing of acrylic fibres is the method of spinning. Depending on the composition of the fibre i.e. the number of co-polymers and depending on whether the fibre is manufactured by the wet process or the dry process, acrylic fibres, differ in their power of absorption of basic dyestuffs and their rate of dyeing.

**Dyeing:** As mentioned before, all acrylic fibres are spun from modified polymers to make them easily dye ability. Besides introducing acidic groups into acrylic fibres, a small quantity of a co-polymer is also incorporated to make the fibre structure loose to facilitate dye ability with disperse dyes and in some cases impart affinity for direct, vat, sulphur and azoic dyes. Acrilan which is modified can be dyed with disperse, basic, acid, metal-complex, chrome, vat, solubilised vat and azoic dyes. The Orion-like fibres are dyed mainly with disperse and basic dyes. The fibres are normally modified to give affinity for basic dyes and a number of basic dyes suitable for dyeing acrylic fibres have been specially developed.

The acrylic fibres can be dyed in the form of loose stock, sliver, slubbing and tow in package dyeing machines taking care to avoid channeling resulting from the thermoplastic nature of the fibre which would lead to uneven dyeing. Yarn is dyed in various yarn dyeing machines in the form of hanks or cheeses. Care is taken to avoid uneven circulation of liquor. For piece dyeing, jiggers are not used as jigger dyeing causes stretching and flattening of the goods and affect the softness and bulkiness of the material. Hence winch machine is used for dyeing woven and knitted fabrics. Acrylic fabrics cannot be heat-set like nylon to give dimensional stability in dyeing. Further, since the material is thermoplastic, it has to be cooled slowly to about 50°C from higher temperatures before taking it out from the dye bath to avoid rope-creases. Drying is also carried out at low temperature because high temperature drying causes discoloration of the material. The goods after drying are usually given a softening treatment. Direct contact with hot metal surfaces is avoided at all stages of processing.

- **Application of Basic Dyes (Cationic Dyes) On Acrylic**

The most important dyes used for acrylic fibres are the basic dyes. These dyes have come into prominence with the arrival of acrylic fibres. Specially developed basic dyes are used for dyeing Orion- like fibres which produce bright and full shades with good fastness to light and washing. They are marketed under various trade names such as Sevron dyes (du Pont), Astra and Astrazon dyes (Bayer), Maxilon dyes (Geigy), Basacryl dyes (BASF), Sandocryl dyes (Sandoz), Deorlene and Deorlene Fast dyes (Ciba), etc.

The main difficulty with basic dyes is that they give uneven dyeings on acrylic fibre if proper precautions are not taken and the dyes are not carefully selected. In the initial stages of dyeing, the uptake of dye is often unlevel and once the dye is taken up by the fibre, it does not come off again so that any unevenness that takes place persists and cannot be rectified. It is, therefore, necessary to control the initial rate of uptake of the dyestuff by the fibre.

These dyes are applied from weakly acid solutions at the boil. Very little dye is taken up by the fibre below 80°C. The absorption of dye rises steeply above 90°C and the temperature has to be raised very slowly from 90°C to 100°C. For obtaining level dyeings, a cationic colorless retarder is added to the bath at 40° to 50°C before addition of the dye. This competes with the dye for the active sites in the fibre and thus retards the exhaustion of the dye in the critical temperature range. The cationic retarders include Tinegal (Ciba), Basacryl Salt G (BASF), and Lyogen BPN (Sandoz). All the basic dyes have a definite saturation value on acrylic fibres; if this is exceeded, the dyed material shows poor fastness to light and washing.

Method of dyeing: Following steps to be followed up for dyeing:

- The dyestuff is pasted with an equal amount of acetic acid (30%) and the paste is diluted 20-30 times of its volume with hot water.
- And dye bath is prepared with required amount of water.
- The pH of the bath set to 5 to 5.5 with acetic acid and sodium acetate (1%).
- Increase the dye bath temperature up $50^{O}$C.
- The dye Solution is then added to the dyebath at this temperature.
- And 4% retarder and 5- 10 % Glauber's salt are then added for obtaining level dyeing.
- The temperature is raise quickly in 15 minutes to $80^{O}$C.
- And controlled between $80^{O}$-$90^{O}$C.
- And it is slowly raised between 90°-100°C i.e. in 40 minutes.
- The dyeing is continuing at this temperature for 1-2 hours.
- The dye bath is cooled slowly to $50^{O}$C.
- Material is rinsed.

Dark dyeings are treated in a bath containing 1 gm/liter dispersing agent like Ultravon JF at 60°- 80°C for 15 minutes for removing any loose dye on the surface which would lower the fastness to washing and rubbing. If shading is required, the bath is cooled slowly to 70°C, additions made and then the temperature raised slowly to the boil.

### Defitherm Process for Even Dyeing In Acrylic Material

BASF has developed an important process called the Defitherm process for even dyeing of acrylic fibres with basic dyes. In this process, the fibres are dyed at a constant defined temperature whereby the unevenness due to temperature differences is eliminated. The difference due to concentration of the dyestuff is also eliminated by adding the dye in as concentrated a form as possible at the prescribed dyeing temperature. The goods are dyed at a specific temperature which is determined by means of bath exhaustion time. A quaternary ammonium compound defithermol TR is added to the bath it act as a retarding agent and thermo regular. It has also a definite exhaustion on the fibers. The addition of this product become necessary only when the dyeing at a calculated temperature say, T60 (the temperature at which the bath exhausts in 60 minutes) is prevented for some reasons. The dyeing temperature T60 can be raised to a higher value with Defithermol TR i.e. the fibre can be dyed at a higher temperature and the dyebath exhausted within 60 minutes by using Defithermol TR.

Defitherm Tables contain data regarding (i) Defithermol TR equivalent of basic dyes (ii) saturation values of different acrylic fibers (iii) initial dyeing temperature and (iv) Actual dyeing temperature.

Method of dyeing: In the actual method of dyeing, the bath is set with acetic acid and water to give a pH of 4.5. The material is entered in the bath and the temperature raised quickly to that required to give Tx (from the tables) and the liquor circulated for 5 minutes. The dyestuff and Defithermol TR are then added in concentrated form and the dyeing is continued for x (time is as per table given by the

Defitherm table) minutes until the bath is exhausted; the temperature is controlled accurately to ± 1°C. After exhaustion the bath is heated to 100°C and the dyeing continued at this temperature for 15 to 30 minutes.

## Dyeing retarders

The presence of either cationic or anionic auxiliary products in the dyebath controls the rapid strike and high rate of dyeing of cationic dyes on acrylic fibres. Cationic retarders are organic ammonium salts with hydrophobic chains. Their adsorption on the fibre surface reduces the negative surface potential. They also compete with the cationic dye for anionic sites in the fibre, thus slowing the rate of adsorption. They have moderate substantivity for acrylic fibres and may even be adsorbed before the dye is added to the bath to decrease the strike. During dyeing, the cationic auxiliary in the fibre is gradually displaced by the cationic dye. Boiling in the presence of some cationic retarder may give some degree of levelling although this invariably increases
the risk of damaging the thermoplastic material. Other types of retarder are cationic polymers that adsorb on the surface of the fibres, decrease the negative surface potential and prevent easy passage of the dye into the fibre.

Anionic retarder’s complex with the cationic dye in the bath (Scheme 18.2) and decrease the number of free dye molecules in solution. Such anion–cation complexes easily precipitate and an anionic agent may have a non-ionic component to keep the complex in dispersion. They are less widely used than cationic retarders. Boiling a dyeing in a blank bath containing an anionic retarder will remove some dye. For complete stripping, bleaching with hypochlorite in the presence of acetic acid at around pH 6 is possible

# MODULE – I

# DYEING OF MAN MADE FIBRE AND THEIR BLENDS

## 1.6 DYES USED FOR MAN MADE FIBRES

Dyes may be defined as the different types of colouring particles, differ each type from other type in chemical composition and are used for colouring fabrics, yarns in different fine of colors and shades and which are completely soluble in liquid substance. They are colored organic compounds that are used impart color to various substrates.

There are different types of dyes for **dyeing** textile goods. These dyes have different nature in fiber. It depends on fiber characteristics, chemical structure etc. The main classes of dyes most widely used for manmade fibre are as follows:

4. Acid dyes
5. Disperse dyes
6. Basic dyes

### 4. Acid dyes

#### *Non-metallised dyes*

These dyes can be applied to nylon, wool or silk in the pH range 3.0–7.0. The wet-fastness of these dyes varies from moderate to good and their light fastness is generally in the blue-scale range 5.0–6.0.

These small relative molecular mass (Mr) dyes are applied at low pH values so that dye–fibre substantivity arises from ion-ion electrostatic forces, for example, in nylon operating between the amino end group, which is protonated under acidic conditions and the anionic dye. Under these conditions the dyes display very good migration and levelling characteristics, but low wet-fastness. Dyes which have larger Mr exhibit higher substantivity for the fibre, but the migrational properties are lower although a higher wet fastness is achieved with these dyes.

These dyes have been divided into three subgroups due to their varying application and fastness properties. Stevens 18 used a I–III grouping for classifying non-metallised acid dyes on nylon:

**Group I:**

Dyes with little affinity under neutral or weakly acidic conditions, but which exhaust under strong acid conditions

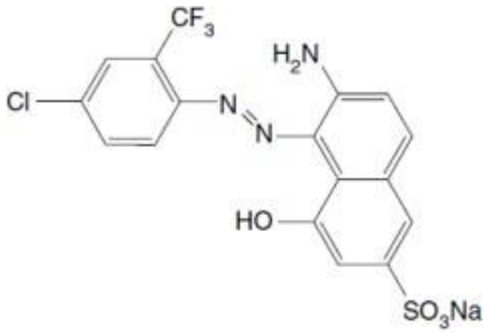
**Group II:**

The largest group of dyes that exhaust onto nylon within the pH range 3.0–5.0.

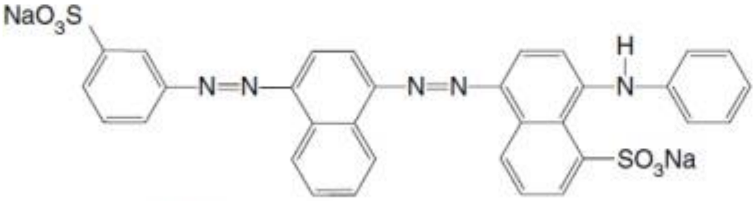
**Group III:**

Dyes that exhibit a high affinity for nylon under neutral or weakly acid conditions (pH 5.0–7.0).

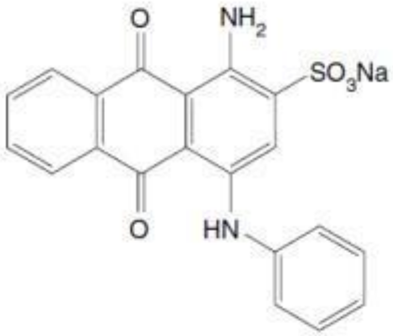
The water solubility of these dyes is due to the presence of one or more sulphonate groups ($-SO_3Na$). These dyes belong to the azo chemical class which represents the largest class of dyes, providing an extremely large gamut of shades. Three examples of these dyes are shown in Figs.



C.I. Acid Red 266 (monoazo).



C.I. Acid Blue 113 (disazo).



C.I. Acid Blue 25 (anthraquinone).

There are several disadvantages associated with non-metallised dyes for some substrates: for example on nylon, low colour yield, lower wet-fastness properties and the tendency to barré dyeing. Also, due to the lower crystallinity of nylon 6 compared to that of nylon 6,6, dyes show a greater rate of uptake on nylon 6 for a given pH range.

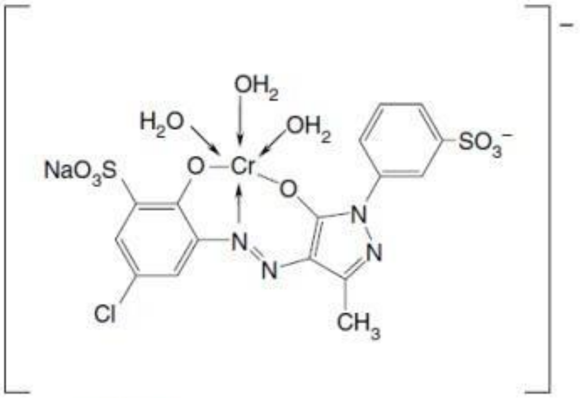
Non-metallised dyes vary in their ability to cover barré nylon. In general low Mr dyes exhibit better coverage than their higher Mr counterparts. Thus by careful dye selection it is possible to greatly minimise or even eliminate the effects of physical variations within the fibre. Eliminating chemical variations is more difficult to achieve.

The limited number of amine end groups (AEG) in the nylon fibre dictates the saturation value of the fibre by the non-metallised acid dyes. Once a dye anion has been attached to an amino group on the fibre, that group is 'neutralised' by the dye anion and so is unable to attract further dye anions.

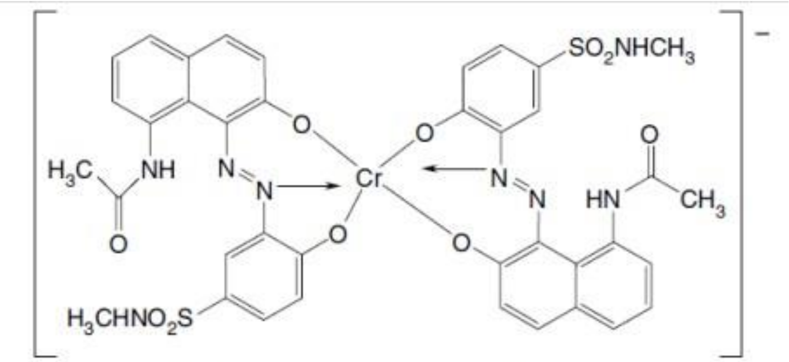
### *Metal-complex dyes*

These dyes are based upon mordant dyes; the difference is that metal complex dyes have the mordant metal incorporated within the dye molecule so do not require a separate mordanting stage. There are two classes of metal-complex dyes – 1:1 metal-complex and 1:2 metal-complex dyes. As the names suggest, the metal-complex dye comprises one metal atom (usually chromium) coordinated with one or two molecules of a dye ligand. An example of each metal-complex structure is shown in Figs.

The 1:1 metal-complex dyes are applied under strongly acidic conditions for satisfactory migration to take place. These conditions can cause severe degradation of nylon fibres and this limits the use of these dyes for dyeing nylon. A few dye manufacturers have tried to overcome this problem by either using sulphamic acid in place of sulphuric acid or by the inclusion of a levelling agent to reduce fibre damage.



C.I. Acid Red 183 (1:1 metal-complex).



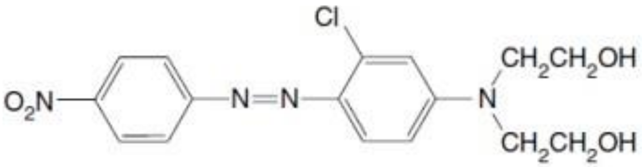
C.I. Acid Black 60 (1:2 metal-complex).

The 1:2 metal-complex dyes exhibit high saturation values and excellent compatibility in mixture shades and they have good light-fastness and . fastness properties. However, their ability to cover chemical variations within the fibre varies significantly and is dependent upon molecular size and substituent solubilising groups. The shade gamut of these dyes is restricted to dull shades and the class is deficient in bright blues and reds. There is a wide range of 1:2 metal-complex dyes available for nylon; different manufacturers' ranges differ in optimum pH range but they are generally applied from a neutral to weakly acidic dye bath.

## 5. Disperse dyes

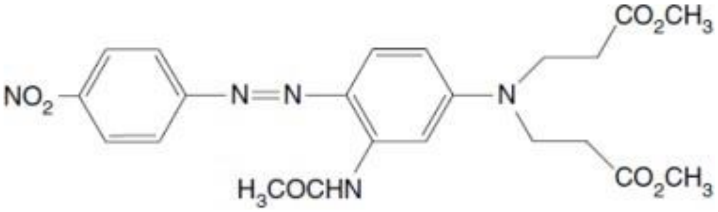
These dyes are frequently insoluble or sparingly soluble in water, non-ionic in character and applied to hydrophobic fibres from an aqueous dispersion. They are predominantly used on polyester but have found application to nylon, cellulose acetate and acrylic fibres, although some of the wet-fastness properties of the dyes on these substrates are poor. The dyed substrate is usually given a reduction clear following dyeing, in order to clean the substrate surface of dye that would cause staining if left untreated.

These dyes were traditionally applied to polyester at the boil with the inclusion of a carrier in the dye bath to facilitate diffusion of the dye into the substrate. Carriers caused many problems to the dyer including residual smell of carrier on fabrics and reduced light-fastness of dyed fabrics due to residual carrier. Since the advent of pressurised dyeing machines, these dyes are now applied to polyester without carriers at temperatures around 130°C; the reduction clear is still conducted after dyeing. A typical disperse dye structure is shown in Fig.



Chemical structure of a disperse dye (C.I. Disperse Red 7).

The ***reduction clear*** is an extra cleaning step which increases processing time and cost together with adding to the effluent load from the dyeing process. There have been attempts to create dyes that become water-soluble in mildly alkaline conditions in order to eliminate the reduction clear process. The Dispersol C dyes from DyStar are one such brand. These dyes had either a sulphonyl fluoride
Or, more commonly, a number of carboxylate ester groups on the molecular structure of the dye. During alkaline scouring after dyeing these groups are converted to their water-soluble sulphonic/carboxylic acid forms rendering the dyes water-soluble, therefore dye which was still on the surface of the substrate would be dissolved in the wash-off liquor and the result would be a clean surface of the substrate. An example of the Dispersol C dyes is shown in Figure.



Chemical Structure of an alkali-clearable disperse dye (C.I. Disperse Red 278)

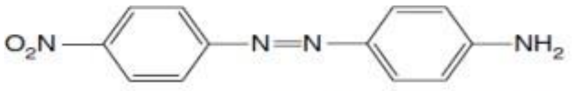
Disperse dyes have also been used in thermal transfer printing. This can be conducted using several methods.

***Pad thermofix***

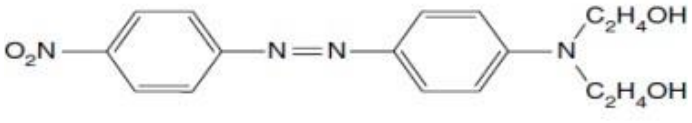
The fabric is padded with dye dispersion and following drying, subjected to a high temperature for a short duration (typically 30–60 s) whereby the dye diffuses into the substrate. The selection of dyes able to undergo sublimation is critical for this process; this rules out the use of the ‘high energy’ type
Of disperse dyes.

***Paper transfer printing***

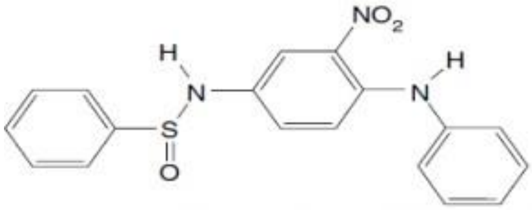
The design required is printed in reverse on a transfer paper. The paper is placed firmly against the substrate which passes between two pressurized heated rollers. The design on the paper is transferred to the substrate via sublimation of the dyes.



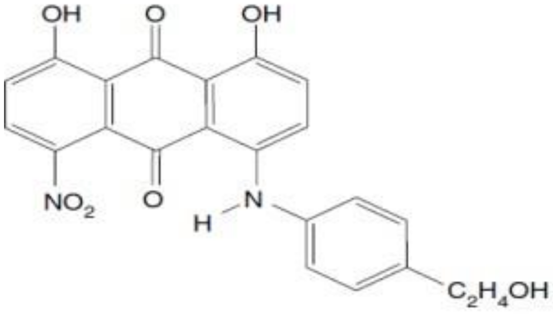
Class A disperse dye (C.I. Disperse Orange 3).



Class B disperse dye (C.I. Disperse Red 19).



Class C disperse dye (C.I. Disperse Yellow 42).

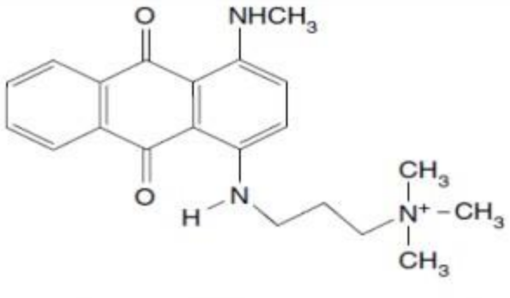


Class D disperse dye (C.I. Disperse Blue 27).

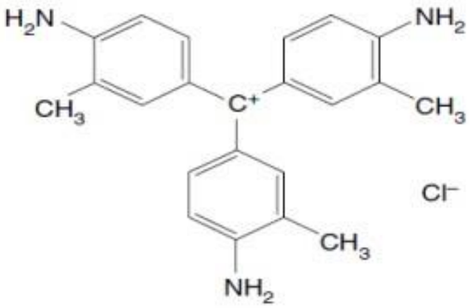
Disperse dyes are classified by their sublimation temperature: Class A dyes have the lowest sublimation temperature whilst Class D dyes have the highest sublimation temperature. The sublimation temperature is also relative to the molecular size of the dyes. Class A dyes are relatively small in molecular size whilst Class D dyes are significantly larger than Class A dyes. Examples of disperse dyes from Class A to Class D dye are shown in Figs.

**6. Basic dyes**

These dyes are usually applied to acrylic, paper and nylon substrates, but can also find use in some modified polyester substrates. Basic dyes are



Localised charge basic dye (C.I. Basic Blue 22).



Delocalised charge basic dye (C.I. Basic Violet 2).

Water-soluble and produce coloured cations in solution; these cations are attracted electrostatically to substrates with a negative charge. Basic or cationic dyes can have either the positive charge localised on an ammonium group (these dyes are characterised by a high tinctorial strength), or it can be distributed as a delocalised charge over the dye cation as found in many triarylmethane, xanthenes and acridine dyes. Examples of a localised and a delocalised charge dye are given in Figs. 1.26 and 1.27, respectively.

Basic dyes are often applied with retarders due to their poor migration properties at the boil. This poor migration is due to the high substantivity of the dye for the substrate and rapid increase in diffusion at high temperatures. Careful control is necessary when using retarders so that anionic sites within the substrate are not blocked which would restrict dye uptake making it difficult to achieve dark shades.

## 1.7 DYEING OF POLYESTER WITH DISPERSE DYES

### c. Brief description of structural parameter of polyester making it difficult to dye.

**Introduction** – Of all the manmade fibers polyester fiber is known in the trade as Terene, Dacron etc. is the most widely used synthetic fiber and its blend with cotton and wool almost popular for dress material.

Chemically polyester is a polymer of an ester obtained by condensing Terephthalic acid with ethylene glycol. Both the raw material is obtained from petroleum products.

**Structural parameter of polyester making it difficult to dye** – Polyester present more difficulties for dyeing at normal dyeing conditions because the polymer chains in polyester are much more closely packed than those in cellulose acetate. The dye stuff particles of dye therefore, don't easily penetrate the fibers and in fact, the process of diffusion of dye is so slow that it takes Week to dye polyester fiber at a temperature of 85ºC.

The dyeing of hydrophilic fibers like cotton and wool is not as difficult as the dyeing of hydrophobic fibers like polyester. The hydrophilic fiber swell on wetting with water and the dye solution taken up by them, occupies the amorphous region in the fiber molecule .And by increasing the temperature the dye molecule diffuse faster in to fiber structure.
In case of hydrophobic fiber water does not swell the fiber because of the following parameters –

1. **High degree of orientation** – The polyester fiber having high degree orientation because of that the dye molecule are not able to diffuse inside the structure of polyester fiber at normal dyeing condition .
2. **High cohesive forces**- The macromolecule of polyester are connected to each other by strong cohesive forces. That's why it is difficult to dye at normal dyeing condition. Dye molecule unable to diffuse between them because of high cohesive force.
3. **Compact structure** –The fiber structure is so compact because of that water is not able to swell the fiber and result negligible amount of water is imbibed in the fiber structure .in sort no space between micro molecules.

### d. Need principle and method of heat setting of polyester.

The stabilisation of dimensions of synthetic fabric is by exposure to heat is possible because of one peculiar property of these fibers namely, that the fiber resist shrinkages at high temperature (below melting point) if they are held at these temperature for a short period of time thus it become dimensionally stable. This operation is crucial for fabrics made of synthetic fibers, for triacetate, and partly for PAC fibers, since it grants excellent dimensional stabilisation and crease proof properties, maintained till the fabric is exposed (by air blowing) to temperatures exceeding the heat setting one. After being treated with water at a temperature above the second order glass transition temperature i.e. 80-85°C for acrylics.

**Need of heat setting** –Heat-setting is a heat treatment by which shape retention, crease resistance, resilience and elasticity are imparted to the fibers. It also brings changes in strength, stretchability, softness, dye ability and sometimes on the colour of the material. All these changes are connected with the structural and chemical modifications occurring in the fiber.

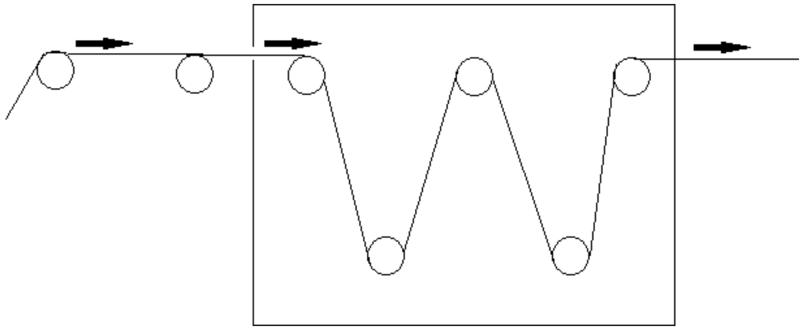
**Stages of Heat Setting-** Heat-setting can be carried out at three different stages in a processing sequence i.e. in grey condition; after scouring; and after dyeing. The stage of heat-setting depends on extent of contaminations and types of fibers or yams present in the fabric. Heat setting after dyeing could lead to the sublimation of disperse dyes (if not accurately selected).Heat setting is carried out on gray fabrics, on scoured fabrics (frequently applied) and on dyed fabrics (scarcely applied). The process grants excellent dimensional stability and good crease-proof properties. As far as operating conditions are concerned, the fabric must be treated in accurately controlled moisture and temperature conditions. Polyester fabrics can be dimensionally stabilised by heat setting at a specific temperature so that they don’t undergo any change in dimension in subsequent processing such as washing or dry cleaning .heat setting consist essentially of exposing the fabric while under dimensional control to a temperature 30$^{o}$C to 40$^{o}$C above the temperature likely to be encountered in its subsequently processing or use. Accordingly for fabrics which are intended for apparel wear and which may be ironed a temperature of 220$^{O}$C to 230$^{O}$C is suitable setting temperature. This process make the fabric stiff but this stiffening is removed in subsequent processing sometime the fabric is even heat set before scouring so that the stiffness of the fabric disappears in processing .if the fabric is not heat set very troublesome creases appears on washing which are difficult to remove.

**Method s of Heat setting –**

- **By Stenter machine.**
- **By curing chamber.**

(Mostly dry heat or radiant heat is preferred for heat setting sometimes steam is also used)

**Stenter Machine-**Stenters is widely used for stretching, drying, heat-setting and finishing of Fabrics. The stenter frame is usually 80-100 feet long and 70-100 inches wide. The speed ranges from 10-45 m/min with a maximum setting time in the setting zone 30 sec at temperature ranging from 175 to 250$^{o}$C depending upon the thickness and type of the material.



Chamber where temperature is maintained as per requirement (175-250$^{o}$C) and speed ranging from 10 - 40 meters per minute. Mostly for heat setting dry air is preferred but some time steam is also preferred in but this method is undesirable as it causes some hydrolysis of the ester groups in the polymer chain due to that material loss its strength.

Stenter machine in heat setting

## Approaches for dyeing, various methods of dyeing polyester involving use of chemical and thermal energy (careers dyeing and, HTHP)

### Approaches for dyeing-

The difficulties, in dyeing were overcome by Ellis who invented the S.H.A. colors' which are applied from an aqueous dispersion (and not from a solution) which has greater affinity for the fiber than the water in the dye bath. Thus the disperse dye migrates from the liquor and dissolves in the fiber. This method is called disperse dyeing and has been used on almost every new fiber that has been developed. Polyester presents more difficulties than other fiber because the polymer chains in polyester are much more closely packed than those in cellulose acetate. The dyestuff particles of disperse dye, therefore, do not easily penetrate the fibers and in fact, the process of diffusion of the dye is so slow that it takes weeks to dye polyester fiber at a temperature of 85°C. The dyeing of hydrophilic fibers like cotton and wool is not as difficult as the dyeing of hydrophobic fibers like Polyester. The hydrophilic fibers swell on wetting with water and the dye solution taken up by them occupies the amorphous region in the fiber molecules and by increasing the temperature the dye molecules diffuse faster into the fiber structure. In the case of hydrophobic fibers, water does not swell the fibers because of their compact structure and when the fiber is entered into the dye bath practically no water enters the fiber structure; the dye molecules do not diffuse into the fiber and the dyeing is, therefore, difficult. This difficulty in dyeing has been overcome by adopting four different methods as under:

**By suitable dye –** by using selected disperse dyes have very small molecular size which can readily diffuse in to fiber structure.

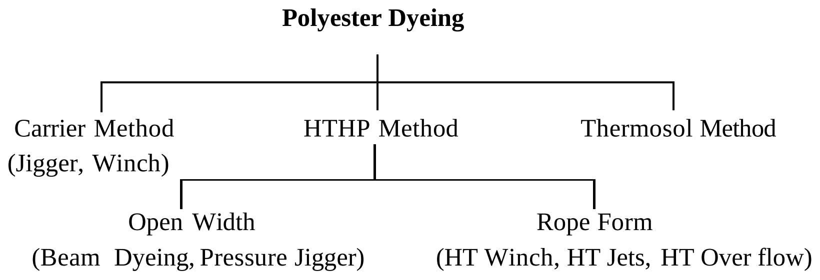
**By opening of fiber structure –**there are two different methods are available for loosen up the fiber structure or opening up of fiber structure

- **By Temperature**- the molecular structure of polyester opened up at high temperature means the bonds get weak and dye molecule get diffuse in to the internal structure of polyester. (180-230$^{o}$C depends on material quality and manufacturing specifications).
- **By chemical (carriers or swelling agent) –** By the help of chemicals like carriers the structure of polyester are also opened at lower temperature. The swelling action of carriers causes diffusion of due molecule easily in to the fiber structure.

**By modification of dyeing technique –** by modifying the technique of dyeing to bring about easy diffusion of the dye molecule directly in to fiber by a process known as thermosol Dyeing Technique. Now a day's mostly HTHP machines are preferred for dyeing of polyester.

## Various methods of dyeing of polyester –

## Polyester Dyeing



## 4. Carrier Method:

Certain chemicals called carriers are added to the dye bath; they are in fact the swelling agents for the fibers. They swell the fiber at boil enabling the chain molecules to move about more easily and increase the distance between them so that there is more space to accommodate the dyestuff molecules. The swollen fibres permit large dye molecules to diffuse more rapidly in the fiber. Thus the carriers increase the solubility of the dye and the rate of dyeing and are absorbed by the fiber. Some of the chemicals used as carriers are; O-phenyl phenol, P- phenyl phenol, dichlorobenzene (Tumescol BDN of lCl), trichlorobenzene (Dilatin TC of Sandoz), dimethyl terephthalate etc. The carriers enable dyeing to be carried out at boiling temperature without the use of special equipment such as high pressure vessels which are expensive.

The carrier is usually added first or is added slowly during the dyeing process because if it is added at once, the dyestuff may rush on to the material.

### (a) Method of dyeing Using Tumescol OP (0-phenyl phenol) as Carrier:

The dyebath is set with 1 gm/l Lissapol D, 0.75 gm/l Dispersol AC, and 3 to 5 gm/l Tumescol OP at 40°-60°C. The material is worked in the blank bath for 15 minutes taking care to see that the carrier gets uniformly absorbed. The well dispersed dye is then added and the temperature raised to boil within 30 minutes. The pH of the bath is maintained 6.5 to 7 by adding 1 ml/l acetic acid for liberation of phenol. The dyeing is continued at boil for 2 hours.

The material after dyeing, is rinsed and soaped at boil with 2 gm/I Lissapol D and 2 to 5 ml/l caustic soda (72°Tw) at 80° -85°C for half an hour to remove residual carrier, this is important as its presence impairs the fastness to light of the dyed material and it causes irritation of the skin and gives unpleasant odour. The last traces of the carrier can be completely removed by curing at 190°C to 200°C for one minute when it sublimes.

### (b) Method of Dyeing with Dilatin B or Dilatin C as carrier:

Dichlorobenzene marketed as Tumescol BDN (by ICI) and as Dilatin B (by Sandoz) and trichlorobenzene marketed as Dilatin C (by Sandoz) can be used for dyeing as under: The dyebath is set with 1 gm/l Ultravon W and the goods are run for a short time at 50°C. 3 to 5 ml/l carrier and 1 ml/l acetic acid (40%) are then added and the goods run in the blank bath for 15 minutes; the dye is then added at 60° to 70°C and the temperature of the bath is raised to boiling point within 30 minutes and dyeing continued at boil for 2 hours. The goods are then rinsed, treated with 1 gm/I Ultravon W at boil and washed.

**The carrier dyeing method has certain advantages as well as disadvantages. The advantages of carrier dyeing method are that:**

- The material can be dyed at atmospheric pressure without using any special equipment.
- The carrier helps the dyestuff in penetrating the fibre.
- The dyeing can be carried out comparatively rapidly and
- The dyeing is more or less uniform.

**The disadvantages of Carrier dyeing method are:**

- The carriers are costly; the cost of dyeing is, therefore, considerable.
- The goods retain the odour of some of the carriers if not washed thoroughly.
- The light fastness of the dyeing is badly affected.
- It is difficult to remove the carrier completely from the dyed material; residual carrier can cause irritation of the skin.
- The process of dyeing is rather lengthy.

**Reduction Clearing**: When the dyeing is not carried out properly or when dyeing a heavy depth of shade, loose dye may get deposited on the fibre after dyeing. This deposition leads to poor fastness to rubbing; hence it has to be removed. This is done after dyeing and before soaping by what is known as the reduction clearing treatment.

The dyed material is treated in a bath containing:

2 to 3 gm/l Lissolamine A (or Dispersol .VL) 6 ml/l caustic soda (68°Tw) and
2 gm/l sodium hydrosulphite at 50°C for 30 minutes and rinsed.
If the material is dyed at a temperature above 100°C it is treated in a bath containing

7 gm/l Dispersol VL (or 3 gm/l Lissolamine RC) 3 gm/l caustic soda flakes and
2 gm/l sodium hydrosulphite at 85°C for 30 minutes, soaped, washed and dried.
The above treatment removes the dyestuff which lies on the surface of the fibre but does not remove that which has penetrated into the fibre.

### 5. High Pressure High Temperature (HTHP) Dyeing

The disperse dye stuffs without the use of carriers do not penetrate (or partly penetrate) the polyester fiber even at 100°C and give only pale shades as most of the dye stuff is located on the surface of the fibers. If however, the temperature is raised beyond 100°C say, to 120°C, the chain molecules in the fibre are much freer to move and the fibre swells to a greater extent. As a result there is rapid penetration of the dyestuff molecules in the fibre structure. The dyeing time is also reduced due to faster diffusion of the dye in the fibre. The fastness properties of the dyed material are improved due to better penetration of the dye and the disadvantages of carrier dyeing are eliminated. The process, however, involves the use of pressure equipment since water dye baths cannot be maintained at a temperature above 100°C at atmospheric pressure. The dyeing has therefore, to be carried out at high pressure and high temperature in closed vessels.

**Method of Dyeing:** The method of dyeing is quite simple. The dyebath is set with 1 gm/I dispersing agent and made acidic with 1 ml/I acetic acid (40%) to bring the pH of the liquor 5.5 to 6. If the dyebath is alkaline, loss of strength of the fibre occurs at high temperature. The goods are entered at 60°C in the pressure vessel and the temperature raised to 130°C quickly. The dyeing is carried out at this temperature for 30 minutes for pale shades and for 1 hour for dark shades. The liquor is then run off and the material is rinsed. If it has been dyed a heavy shade it is given a reduction clearing treatment and it is then soaped with 1gm/l Lissapol D at 80°C for 30 minutes, rinsed again and dried.

### 6. Thermosol Method of Dyeing

This process was developed by du Pont in 1949 for dyeing polyester with disperse dyes without using carriers. The principle of this method is that polyester fibres which are thermoplastic soften when heated to high temperature and many disperse dyes at that temperature melt with the result that the molten dye dissolves in the fibre which itself is in a plasticized or viscous state. In the actual process, the dye is applied by padding from an aqueous medium; the fabric is dried to remove water thereby leaving the dye on the surface of the fabric. After drying, the fabric is exposed to a high temperature (205°C) for a minute during which the dye "dissolves" in the fibre and becomes so fast that it cannot be removed even by most severe laundering. Any unfixed dye is then removed by reduction clearing. Yarn in the form of skeins or hanks can also be dyed by this method by using a simple yarn padder. The hank is padded with a fine dispersion of the dye, squeezed, dried, stretched and then cured at 205°C for a minute.

The fabric is heat-set before dyeing. It is then padded on a three bowl padding mangle with two dips and two nips. The padding liquor contains 3 to 4% CMC or 2 gm/l sodium alginate thickener (1:4) to ensure even dyeing and prevents dye migration; the pH of the bath is adjusted between 6.5 and 7 with 12 gm/l mono sodium di- hydrogen phosphate ($NaH_2PO_4$).

A volatile solvent like butanol is also added to the padding liquor to assist uniform spreading of the dye on the fabric surface. The padded fabric with 60% pick-up is then carefully dried. Uniform drying is the most important step in this method. Slow and even drying is essential.

In the conventional drying equipment, the moisture is removed from the surface of the fabric as vapour as a result of which more water is drawn to the surface from the interior of the fibres; due to this internal movement of water migration of dye takes place. There is also a difference in the rate of drying between the two sides of the fabric which leads to two-sided effect. Infra-red drying which eliminates dye migration is the most suitable method. Due to radiant heat, water is evaporated not only from the fabric surface but also from within the fibres and the drying is uniform. The moisture content of the fabric is reduced from 60% to 30% by radiant heat. The fabric is then further dried on a range of 14 steam-heated cylinders the first 4 of which are coated with Teflon to prevent sticking. The fabric is then cured in a curing oven or stenter or in hot roll equipment at 205°C for 1 minute, whereby 75 to 90 % of the dye is fixed. During heating the fabric has to be kept free from wrinkling and both the sides of it have to be heated uniformly.

The Thermosol range consists essentially of a padder, an infra-red drying unit, a cylinder drying range, a hot flue thermosol oven, a steaming unit, an open soaper and washing tanks.

This process can be applied to polyester-cotton blended fabrics also. The polyester component is first dyed on the thermosol range with disperse dyes and then the cotton component is dyed with suitable dyes on a pad-steam range.

**Advantages of this process are:**

- No carrier is requires in dyeing; hence the high cost of carrier and its adverse effect on light fastness of the dyed material are eliminated.
- It is a continuous process; therefore, large quantities of the material can be dyed more economically than by the batch process.
- Most of the dye i.e. 75 to 90 % is fully utilized in dyeing;

## 1.8 DYEING OF CATIONIC DYE-ABLE POLYESTER FIBRE

Cationic Dyeable Polyester is a special Polyester fiber which has undergone a change during polymerization. They were built of molecules of 5 - sulphophthalic acid, to generate anionic sites that the fibers of normal PET not have. Having anionic groups it can also be dyed with cationic dyes with results of high brilliance. However, these fibers can be dyed with disperse dyes. Compared to ionic dyes, disperse dyes have smaller molecular extinction coefficients and lower build-up property, so these dyes cannot give bright and deep colors. This type of fibers were born also to lower the Tg (glass transition temperature) of the polymer, 10 ° C lower than normal Polyester fibers, so to obtain a more segmental mobility and open polymer structure. Resulting in increased rate of diffusion of the dye in the fiber at a lower temperature. Tg Range (70 – 85°C). This modified polymer is also more easily hydrolised and more sensitive to heat setting before dyeing at a maximum temperature of 180°C.

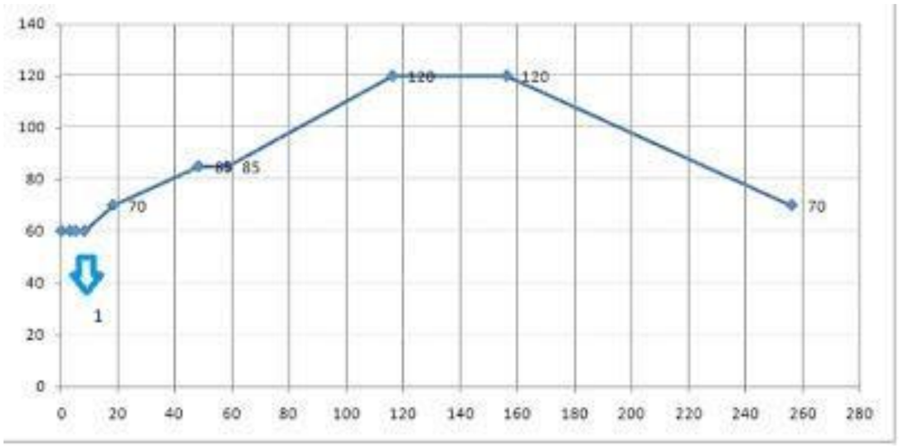
**Example**

Scouring and dyeing exhausted process in Overflow – Jet Machine (Liquor ratio - 1:10 – 1:20) :
Scouring:
Continuous washing cold for 10 min
Drain well (for water soluble oils)

Fill with water 30 ° - 35°C
0,5 g/l Antifoam (preferably non-silicone) alone
1 g/l Detergent non – ionic
0,5 g/l Caustic Soda 36° Bè
Raise to 80°C quickly and hold for 20 – 25 min
Drain well
washing cold for 10 min and after starting in dyeing.

**Dyeing with Cationic dyes**

Follow the Graph below :



The dye bath is set at 60°C - introduce order
0,5 g/l Antifoam (alone)
8 g/l Sodium sulphate (only dyeing at 120°C) (1)
1 g/l Dispersant non-ionic
X g/l Acetic Acid pH = 4,5

X % Levelling – Carrier anionic (only dyeing at 98°C)
X% Cationic dyes (dissolved at 60°C with 1 g / l of acetic acid) - (introduce preferably dosed curve progressive Sen +)

Then raise to 70°C - after to 85°C at 0,5°C / min (while the fiber is softening) and hold for 10 min, after raise to 120° (or 98°C) at 0,6°C / min – hold for 30 – 60 min (depends on the depth of the color)
then cool to 70°C at 0,5°C / min and check the color.

Please note that sodium sulphate (Na +), being very stable at high temperatures, is the protector of te anionic sites sensitive to the acid at 120 °C.

After dyeing, the dyed samples were rinsed and washed with 2 g/l of non-ionic detergent at 60 – 70°C.
**Light fastness:** moderate to good
**Wash fastness:** good to excellent
**Rubbing fastness:** good
Excellent resistance to **sublimation** on wet
No fouling of lycra mixed

## 1.9 DYEING OF POLYESTER /COTTON AND POLYESTER /WOOL BLENDED FABRICS WITH SUITABLE DYES.

### DYEING POLYESTER /COTTON BLENDS

### Introduction

There is a major market for 65/35 and 50/50 polyester/cotton fabrics for a varietyof end-uses, in weights ranging from light shirting to heavy industrial fabric. A variety of different batch and continuous dyeing processes are used for these. The dyeing of blends of polyester with other cellulosic fibres such as viscose and linen follows much the same principles outlined here, although there are some slight differences in the actual details.

The dyeing properties of polyester and cotton fibres are quite different and most of the dyeing methods for their unions involve separate steps for the colouring of the two fibres. The polyester component is invariably dyed first with a mixture of disperse dyes. For the cotton, there is a choice of dyes, the actual selection depending on the desired colour, the type of finishing required, the demanded fastness properties, the costs and the type of machinery available. The cotton is usually dyed with reactive, direct, sulphur, vat, or azoic dyes. The use of the latter three types is decreasing because of increased costs and environmental problems.

The reactive/disperse dye combination for dyeing cotton/polyester clothing fabrics is very popular. If the cotton is dyed first, subsequent pressure dyeing of the polyester at 120–130 °C can change the shade of the dyed cotton because the cotton dyes are less stable at high temperatures. Dyeing the polyester before the cotton allows an intermediate reduction clearing of any disperse dye on the polyester surface or remaining in the cotton (Section 15.7.4). An alkaline solution of hydros destroys several types of cotton dyes so that reduction clearing is precluded after dyeing the cotton. In addition, once the polyester is dyed any detrimental effects of required cotton dyeing assistants such as alkali and salt on the disperse dyes are avoided.

Cross-staining of the cotton by disperse dyes can be a problem. The stained cotton has poor light and washing fastness and the weakly held disperse dyes will transfer colour to other synthetic fibres such as nylon during washing. For deep shades, alkaline scouring, or preferably reduction clearing with alkaline hydros and a non-ionic detergent, removes the disperse dyes staining the cotton. Because cotton crosslinking agents used in the finishing of cotton/polyester fabrics require the use of relatively high curing temperatures, the disperse dyes used for the polyester must be of the types that have higher sublimation fastness. Therefore, high-energy disperse dyes are preferred. For fabrics with more than 60% polyester, the cotton component may not even be dyed if the required shade is only pale and the two fibres are well blended in the yarn.

As always, careful fabric preparation is essential for production of high quality dyeings. The aim is to produce a fabric that is easily wetted and absorbs dyes as uniformly as possible. It is imperative that singeing does not produce small masses of melted polyester on the fibre ends since these tend to dye more deeply than the fibres resulting in a fabric with a spotty appearance. Heat setting the polyester before dyeing, to stabilise the fabric dimensions, must be uniform since it influences both the rate and extent of dyeing with disperse dyes. Heat setting after dyeing helps to remove creases in the fabric and to set its final dimensions. It can, however, cause thermal migration of the disperse dyes in the polyester fibres. In the case of poorly penetrated fibres, disperse dyes may migrate further into the polyester fibre interior, thus deepening the shade. Alternatively, if any hydrophobic chemical such as non-ionic surfactant or fabric softener remains on the polyester fibre surfaces, disperse dyes may migrate into this layer, in which they are very soluble. This results in greater ease of colour removal by washing or rubbing during use, and is undesirable.

In many cases of union dyeing, the dyes and dyeing conditions for colouring one of the fibres influence the other fibre and its dyes. The major areas of concern are:

(4) the degree of cross-staining. Although disperse dyes will stain cotton, the anionic cotton dyes usually completely reserve the polyester. The disperse dyes selected should be those that give minimal cotton staining;

(5) interactions between dyes and auxiliaries when present in the same bath. For example, many disperse dyes are not stable under the alkaline reducing conditions used in leuco vat dyeing. The salt and alkali required for dyeing cotton with reactive dyes often have a deleterious effect on the dispersing agent for disperse dyes and cause particle aggregation;

(6) the conditions for fixation or aftertreatment of one type of dye on the other types often limits the processing methods that are possible. Thus, if direct dyes are used for continuous dyeing in combination with disperse dyes they must be stable to the high temperatures used in the Thermosol process. This factor influences when reduction clearing can be used. It is not possible to clear disperse dyes staining the cotton with an alkaline hydros solution if the cotton is already dyed. All the types of dyes used to colour cotton will be reduced under these conditions and the colour destroyed.

Even when staple polyester is the predominant fibre in intimate blends with cotton, the cotton fibres have a tendency to migrate to the yarn surfaces and have higher visibility. The colour and the fastness properties of the dyed cotton are therefore important, even though it is the minor component.

One of the major problems in dyeing cotton/polyester fabrics is that of colour control. This is true for cross-dyeings and for solid shades. To examine the colours of the individual fibres after dyeing, they must be separated. This is not easy. For simple evaluation of dyeing, small swatches of 100% polyester and 100% cotton fabrics, with characteristics close to those of the fibres in the blend, can be sewn onto the cotton/polyester material and their colours examined after dyeing. This avoids having to separate the two kinds of fibres. Alternatively, a widely used technique is to evaluate the colour of the dyed blend and then to dissolve out the cotton with 70% aqueous sulphuric acid. The polyester is unaffected by this and a polyester ‘skeleton’ remains, the colour of which can be examined. The colour of the cotton is assessed from the difference between the colours of the original fabric and the residual polyester skeleton.

Because a mixture of dyes is needed for dyeing this type of fibre blend, and because there are a number of potential problems, consultation with a dye manufacturer is recommended in selecting dyes and processes. Suppliers are able to recommend disperse dyes that minimise staining of the cotton, suitable dyes for the cotton, and point out inappropriate dye combinations.

## DYEING POLYESTER /WOOL BLENDS

Fabrics containing a blend of polyester and wool have superior abrasion and crease resistance to those made from wool alone, yet they retain the valued warmth and handle of wool fabrics. In many cases, where the highest quality and good fastness properties are essential, the two fibres may be dyed separately before blending and fabric construction.

The dyeing of wool/polyester mixtures, using acid dyes for the wool and disperse dyes for the polyester, allows the production of solid shades and all types of cross dyeing. In the two-bath dyeing process, the polyester is first dyed with the disperse dyes under pressure at up to 130 °C using a weakly acid dye bath at around pH 5. Dyeing times should be short since the wool is more prone to damage at temperatures above 105 °C. In dyeing wool/polyester unions, the disperse dyes may stain the wool fibres in the blend and the long time required for their migration to the polyester can cause a loss of wool quality. Any residual disperse dyes in the wool must be removed under the mildest conditions possible by soaping with a non-ionic detergent solution at 70 °C. Alternatively, reduction clearing with a weakly alkaline ammonia

solution of hydros or formaldehydesulphoxylate avoids damaging the wool. Acid dyes then dye the wool under weakly acidic conditions in a second bath.

In the one-bath process, fast acid and disperse dyes are applied simultaneously from a weakly acidic dyebath, followed by soaping. In deep shades, staining of the wool by disperse dyes is heavy and unless the soaping treatment is effective, the washing fastness of the dyeings may be inferior. The one-bath dyeing method is useful mainly for pale to medium depths of moderate fastness. Both the acid and disperse dyes are applied simultaneously using a polyester dyeing carrier at the boil at pH 4–5. The use of a carrier avoids the lengthy times for the transfer of disperse dye held by the wool to the polyester. The wool must be cleared of disperse dye by scouring with non-ionic detergent. Reduction clearing is not possible in this case, since the wool is already dyed with dyes sensitive to reducing agents. Alternatively, a one-bath process at 120 °C uses a wool protection agent and there is little cross-staining of the wool by the disperse dye.

## 1.10DYEING OF ACRYLIC WITH BASIC DYES

### Structure aspect of acrylic affecting their dyeing behavior

Introduction: Acrylic fibres which were introduced in 1950 occupy an important place in the synthetic fibre industry. These fibres appeared in our country under the name "Cashmilon" they are marketed under various trade names such as Orion, Creslan, Drelan, Courteiie, and Acrilan etc. When the acrylic polymer was first made it could not be transformed into commercially useful product because suitable organic solvents which could be used for preparing solutions of polyacrylonitrile were not known. The solvents which are normally used such as acetone, ethyl alcohol etc., were of no use. The acrylic fibre became a commercial reality with the discovery in du Pont laboratories of suitable organic solvents for preparing solutions of polyacrylonitrile. A number of solvents have been patented; among these are: dimethoxy acetamide, dimethyi acetamide, dimethyi formamide and the Meta and Para nitro phenols.

Acrylic fibre is prepared by the polymerization by heat or peroxide of acrylonitrile $CH_2$ = CH-CN another name for which is vinyl cyanide. Aciylonitrile is a fairly volatile liquid obtained from ethylene oxide with hydrocyanic acid.

According to the modern process known as the Sohio process, acrylonitrile is made from propylene and not from ethylene oxide because this process is economical. The acrylonitrile monomer alone or together with another monomer selected for co-polymerization is polymerised in the presence of a suitable catalyst at appropriate temperature and time. The polymer is then blended and dissolved in a suitable solvent. The solution is then filtered. The fibre is spun by the wet or dry process. The solution of the polymer is forced through a spinneret into a medium where solvent is removed and the solid filaments are formed. Acrylic fibre possesses a very pleasing, warm and soft handle; fabrics made from it exhibit a silk like luster, hand and drape.

Dyeing Behavior: A 100 % acrylic fiber is very difficult to dye because of its compact structure. This is mainly due to the high glass transition temperature (tg) of the fibre viz. 105°C; this means that the fibres become thermoplastic at or above this temperature. Below this temperature the fibres form a barrier to the approaching dye molecules. However, above the glass transition temperature, the fibre molecules change to a thermoplastic state so that when they come in contact with a dye molecule at this temperature the dye molecules are able to penetrate into the fibre. Fibres made from cent per cent acrylonitrile are not, therefore, used commercially. 85 to 90% of acrylonitrile is co-polymerised with 10 to 15 per cent of a monomer to make the fibre readily dyeable. The commonly used co-monomers in acrylic fibres are vinyl acetate, methyl methacrylate. The addition of co monomers decreases the glass transition temperature of the fiber (from 105°C) and thus increases the diffusion rate of the dyestuff. Most modern acrylic fibres have a tg of about 70° -80°. These fibers are two types

- Those containing acidic groups such as Orion 42 which can be dyed with basic dyes and
- Those containing basic groups such as Acrilan which can be dyed with acid dyes.

The Orlon-type acrylic fibres are more important than Acrilan-type fibres as the former are most widely used. The presence of the co-monomers in the fibres modifies their thermoplastic properties and dyeing properties are improved so that disperse dyes and basic dyes can be applied below 100°C in conventional equipment. Another important factor that affects the dyeing of acrylic fibres is the method of spinning. Depending on the composition of the fibre i.e. the number of co-polymers and depending on whether the fibre is manufactured by the wet process or the dry process, acrylic fibres, differ in their power of absorption of basic dyestuffs and their rate of dyeing.

**Dyeing:** As mentioned before, all acrylic fibres are spun from modified polymers to make them easily dye ability. Besides introducing acidic groups into acrylic fibres, a small quantity of a co-polymer is also incorporated to make the fibre structure loose to facilitate dye ability with disperse dyes and in some cases impart affinity for direct, vat, sulphur and azoic dyes. Acrilan which is modified can be dyed with disperse, basic, acid, metal-complex, chrome, vat, solubilised vat and azoic dyes. The Orion-like fibres are dyed mainly with disperse and basic dyes. The fibres are normally modified to give affinity for basic dyes and a number of basic dyes suitable for dyeing acrylic fibres have been specially developed.

The acrylic fibres can be dyed in the form of loose stock, sliver, slubbing and tow in package dyeing machines taking care to avoid channeling resulting from the thermoplastic nature of the fibre which would lead to uneven dyeing. Yarn is dyed in various yarn dyeing machines in the form of hanks or cheeses. Care is taken to avoid uneven circulation of liquor. For piece dyeing, jiggers are not used as jigger dyeing causes stretching and flattening of the goods and affect the softness and bulkiness of the material. Hence winch machine is used for dyeing woven and knitted fabrics. Acrylic fabrics cannot be heat-set like nylon to give dimensional stability in dyeing. Further, since the material is thermoplastic, it has to be cooled slowly to about 50°C from higher temperatures before taking it out from the dye bath to avoid rope-creases. Drying is also carried out at low temperature because high temperature drying causes discoloration of the material. The goods after drying are usually given a softening treatment. Direct contact with hot metal surfaces is avoided at all stages of processing.

- **Application of Basic Dyes (Cationic Dyes) On Acrylic**

The most important dyes used for acrylic fibres are the basic dyes. These dyes have come into prominence with the arrival of acrylic fibres. Specially developed basic dyes are used for dyeing Orion- like fibres which produce bright and full shades with good fastness to light and washing. They are marketed under various trade names such as Sevron dyes (du Pont), Astra and Astrazon dyes (Bayer), Maxilon dyes (Geigy), Basacryl dyes (BASF), Sandocryl dyes (Sandoz), Deorlene and Deorlene Fast dyes (Ciba), etc.

The main difficulty with basic dyes is that they give uneven dyeings on acrylic fibre if proper precautions are not taken and the dyes are not carefully selected. In the initial stages of dyeing, the uptake of dye is often unlevel and once the dye is taken up by the fibre, it does not come off again so that any unevenness that takes place persists and cannot be rectified. It is, therefore, necessary to control the initial rate of uptake of the dyestuff by the fibre.

These dyes are applied from weakly acid solutions at the boil. Very little dye is taken up by the fibre below 80°C. The absorption of dye rises steeply above 90°C and the temperature has to be raised very slowly from 90°C to 100°C. For obtaining level dyeings, a cationic colorless retarder is added to the bath at 40° to 50°C before addition of the dye. This competes with the dye for the active sites in the fibre and thus retards the exhaustion of the dye in the critical temperature range. The cationic retarders include Tinegal (Ciba), Basacryl Salt G (BASF), and Lyogen BPN (Sandoz). All the basic dyes have a definite saturation value on acrylic fibres; if this is exceeded, the dyed material shows poor fastness to light and washing.

Method of dyeing: Following steps to be followed up for dyeing:

- The dyestuff is pasted with an equal amount of acetic acid (30%) and the paste is diluted 20-30 times of its volume with hot water.
- And dye bath is prepared with required amount of water.
- The pH of the bath set to 5 to 5.5 with acetic acid and sodium acetate (1%).
- Increase the dye bath temperature up $50^{O}$C.
- The dye Solution is then added to the dyebath at this temperature.
- And 4% retarder and 5- 10 % Glauber's salt are then added for obtaining level dyeing.
- The temperature is raise quickly in 15 minutes to $80^{O}$C.
- And controlled between $80^{O}$-$90^{O}$C.
- And it is slowly raised between 90°-100°C i.e. in 40 minutes.
- The dyeing is continuing at this temperature for 1-2 hours.
- The dye bath is cooled slowly to $50^{O}$C.
- Material is rinsed.

Dark dyeings are treated in a bath containing 1 gm/liter dispersing agent like Ultravon JF at 60°- 80°C for 15 minutes for removing any loose dye on the surface which would lower the fastness to washing and rubbing. If shading is required, the bath is cooled slowly to 70°C, additions made and then the temperature raised slowly to the boil.

**Defitherm Process for Even Dyeing In Acrylic Material**

BASF has developed an important process called the Defitherm process for even dyeing of acrylic fibres with basic dyes. In this process, the fibres are dyed at a constant defined temperature whereby the unevenness due to temperature differences is eliminated. The difference due to concentration of the dyestuff is also eliminated by adding the dye in as concentrated a form as possible at the prescribed dyeing temperature. The goods are dyed at a specific temperature which is determined by means of bath exhaustion time. A quaternary ammonium compound defithermol TR is added to the bath it act as a retarding agent and thermo regular. It has also a definite exhaustion on the fibers. The addition of this product become necessary only when the dyeing at a calculated temperature say, T60 (the temperature at which the bath exhausts in 60 minutes) is prevented for some reasons. The dyeing temperature T60 can be raised to a higher value with Defithermol TR i.e. the fibre can be dyed at a higher temperature and the dyebath exhausted within 60 minutes by using Defithermol TR.

Defitherm Tables contain data regarding (i) Defithermol TR equivalent of basic dyes (ii) saturation values of different acrylic fibers (iii) initial dyeing temperature and (iv) Actual dyeing temperature.

Method of dyeing: In the actual method of dyeing, the bath is set with acetic acid and water to give a pH of 4.5. The material is entered in the bath and the temperature raised quickly to that required to give Tx (from the tables) and the liquor circulated for 5 minutes. The dyestuff and Defithermol TR are then added in concentrated form and the dyeing is continued for x (time is as per table given by the

Defitherm table) minutes until the bath is exhausted; the temperature is controlled accurately to ± 1°C. After exhaustion the bath is heated to 100°C and the dyeing continued at this temperature for 15 to 30 minutes.

## Dyeing retarders

The presence of either cationic or anionic auxiliary products in the dyebath controls the rapid strike and high rate of dyeing of cationic dyes on acrylic fibres. Cationic retarders are organic ammonium salts with hydrophobic chains. Their adsorption on the fibre surface reduces the negative surface potential. They also compete with the cationic dye for anionic sites in the fibre, thus slowing the rate of adsorption. They have moderate substantivity for acrylic fibres and may even be adsorbed before the dye is added to the bath to decrease the strike. During dyeing, the cationic auxiliary in the fibre is gradually displaced by the cationic dye. Boiling in the presence of some cationic retarder may give some degree of levelling although this invariably increases
the risk of damaging the thermoplastic material. Other types of retarder are cationic polymers that adsorb on the surface of the fibres, decrease the negative surface potential and prevent easy passage of the dye into the fibre.

Anionic retarder’s complex with the cationic dye in the bath (Scheme 18.2) and decrease the number of free dye molecules in solution. Such anion–cation complexes easily precipitate and an anionic agent may have a non-ionic component to keep the complex in dispersion. They are less widely used than cationic retarders. Boiling a dyeing in a blank bath containing an anionic retarder will remove some dye. For complete stripping, bleaching with hypochlorite in the presence of acetic acid at around pH 6 is possible.

# MODULE – III

# MECHANICAL FINISHING

## 3. MECHANICAL FINISHING

### *3.1 OBJECTS & CLASSIFICATION OF FINISHING*

### *FINISHING:*

Finishing is a series of processing operations applied to a textile material to improve it's appearance, handle and functional properties.

We can also say finishing is a series of processing operations applied to gray fabrics to enhance their appearance and hand, properties and possible applications. Play a fundamental role for the commercial excellence of the results of textiles.

Develop the "product finishing" in all its fundamental elements such as hand and appearance; Give the finished fabric some properties that grant an optimum behavior during the making up and all through the life of the textile.

### *OBJECT OF FINISHING*

- To enhance the suitability of the fabric for end use.
- To improve appearance and sale appeal for comport and utility.

To give desirable qualities to the fabric like-

1. Softness
2. Luster
3. Drape
4. Dimensional stability
5. Crease recovery
6. Soil repellence

More specifically, objects of finishing can be-

- To improve the appearance of the fabric.
- To improve the feel of the fabric.
- To cover faults in the original fabric.
- To improve wearing qualities of fabric by making it shrink or crease resistant.
- To set garment shape. E.g. Durable press.
- To import special properties to the fabric for special end uses such as waterproofing, flame-proofing etc.

- To strengthen the fabric by coating or laminating.
- To produce novelty effects e.g. organdie fabrics by parchmentising

## *CLASSIFICATION OF FINISHES:*

The finishing processes may be broadly classified into two groups:

1. Physical or mechanical finishes
2. Chemical finishes

### *1. Physical or mechanical finishes*

The physical or mechanical processes encompass simple processes like drying on a steam-heated cylinder to various type of calenders, raising for soft effects on the surface of the fabric and breaking the finishing of filled goods for comfortable feel.

Most of the mechanical finishes are known from ancient times and few changes have occurred in their method of operations. Some physical properties, such as dimensional stability, can be improved with chemical finishing.

Mechanical finishing or ‘dry finishing’ uses mainly physical (especially mechanical) means to change fabric properties and usually alters the fabric's appearance as well. The mechanical finishes include calendering, emerising, compressive shrinkage, raising, brushing and shearing or cropping. The mechanical finishes for wool fabrics are milling, pressing and setting with crabbing and decatising. Mechanical finishing also encompasses thermal processes such as heat setting (i.e., thermal finishing). Mechanical finishing is considered a dry operation even though moisture and chemicals are often needed to successfully process the fabric.

### *2. Chemical finishes*

Chemical finishing or ‘wet finishing’ involves the addition of chemicals to textiles to achieve a desired result. In chemical finishing, water is used as the medium for applying the chemicals. Heat is used to drive off the water and to activate the chemicals. The chemical methods have changed with time remarkably, and the newer finishes have been developed continually. Many chemical methods are combined with mechanical methods, such as calendering, to improve the effect. Typically, the appearance of the textile is unchanged after chemical finishing.

Some finishes combine mechanical processes along with the application of chemicals. Some mechanical finishes need an application of chemicals; for example, milling agents are needed for the fulling process or reductive and fixation agents for shrink proofing wool fabrics. On the other hand, chemical finishing is impossible without mechanical assistance, such as fabric transport and product application. The assignment to mechanical or chemical finishing depends on the circumstance; that is, whether the major component of the fabric's improvement step is more mechanical or chemical.

Mechanical devices are used in both categories; the major distinction between the two is what caused the desired fabric change, the chemical or the machine?

Another method of classification is to classify finishes as **temporary and permanent finishes**. In fact, no finish stands permanently till the material is serviceable, hence a more accurate classification would be **temporary or durable**.

***Some of the temporary finishes are:***

- Mechanical: calender, schreinering, embossing, glazing, breaking, stretching, etc.
- Filling: starch, china clay and other mineral fillers
- Surface application: oil, different softeners and other finishing agents.
-

***Some of the durable finishes are:***

- Mechanical: compressive shrinkage, milling of wool, raising and cutting processes, permanent setting, etc.
- Deposition: synthetic resins—both internal and external, rubber latex, laminating, etc.
- Chemical: **mercerisation**, perchmentising, cross-linking agents, water repellent finish, fire-resistant and fireproofing finishes, shrink proofing of wool, etc.

It should be noted that any such classification is arbitrary. Accurate classification is difficult because durability depends on several factors. Durability can be varied, and it is not possible to draw any borderline between temporary and durable finishes.

## *3.2 OBJECTS OF CALENDARING AND WORKING OF DIFFERENT CALENDARS.*

### *OBJECTS:*

To upgrade the fabric handle and to impart a smooth silky touch to the fabric.

- To compress the fabric and reduce its thickness.
- To improve the Opacity of the fabric.
- To reduce the Air Permeability of the fabric by changing its porosity.
- To impart different degree of Lustre to the fabric.
- To reduce the Yarn Slippage

## *3.3. STENTERING & SANFORIZATION*

### *Stenter Machine:*

A machine or apparatus for stretching or stentering fabrics. The purpose of the stenter machine is to bringing the length and width to pre determine dimensions and also for **heat setting** and it is used for applying finishing chemicals and also shade variation is adjusted. The main function of the stenter is to stretch the fabric widthwise and to recover the uniform width.

***Stentering machine***

### Functions of Stenter Machines:

1. Heat setting is done by the stenter for lycra fabric, synthetic and blended fabric.
2. Width of the fabric is controlled by the stenter.
3. Finishing chemical apply on fabric by the stenter.
4. Loop of the knit fabric is controlled.
5. Moisture of the fabric is controlled by the stenter.
6. Spirility controlled by the stenter.
7. GSM of the fabric is controlled by stenter.
8. Fabric is dried by the stentering process.
9. Shrinkage property of the fabric is controlled.
10. Curing treatment for resin, water repellent fabric is done by the stenter.

### *Components of Stenter Machine:*

- Paders
- Weft straightner (Mahlo)
- Burners 10

- Heat recovery
- Attraction rollers
- Circulating fans 10,8
- Exhaust fans 2
- Winder 2
- Clips
- Pins
- I.R
- Cooling drums 2

### *Working Procedure of Stenter Machine:*

The fabric is collected from the batcher to the scray and then it is passed through the padders where the finishes are applied and some times shade variation is corrected.The fabric is entered into the mahlo (weft straigtner) the function of the mahlo is to set the bow and also weave of the fabric is griped by the clips and pins are also provided but the pins has a disadvantage that they pins make holes at the selvedge but the stretchning of the pins are greater than the clips.these clips and pins are joined to endless chain.there are 8 to 10 chambers provided on the machine each chamber contains a burner and filters are provided to separate dust from air.the circulating fans blow air from the base to the upper side and exhaust fans sucks all the hot air within the chambers. Attraction rollers ar provided to stretch the warp yarn.

After stentering we can increase the width of the fabric up to 1.5-2 inch.The speed of the machine is about 7-150 m/min.3 meters fabric can run in each chamber.temperature is adjusted that according to the fabric as for,

1. PC 210 c
2. Cotton 110-130 c

After dyeing 160-170c and after print 130-140c.

### *Comparison Between Stenter 10 F, Stenter 8 F and Knit Stenter:*

**Stenter 10 F:**
The word 10 F stands for 10 flames.in stenter 10 F clips are used to stretch the fabric and this is a disadvantage that holes appears on the selvedge of the fabric and also uneven dyeing is achieved.

**Stenter 8 F:**
Stenter 8 F has 8 flames and the main purpose of 8F stenter same as 10F stenter. The basic advantage of the machine is dyeing can also done on 8F machine and has I.R system. Finishing, dyeing can also done even we can dye pigment , heat setting and also we can control skew and bow problems and another advantage is using light shades no clip marks appears.

***Knit Stenter:***

The basic difference of the knit stenter machine is that it is used for knit fabric weft straightening, heat setting, dyeing, light shades and also for print and knit fiishing chemicals applicaions. Pins are also provided with the clips.flat rollers are present and a brush to hold the pin,the L-guide is also used for knit fabric and a selvedge cutter with suction privided.

***Specification of a Stenter Machine:***

| | |
|---|---|
| **Brand Name** | Bruckner |
| **Serial no** | 72276-0463 |
| **Origin** | Germany |
| **Year of manufacture** | 1995 |
| **Speed range** | 15-30 m/min |
| **Temperature range** | 50-250C |
| **Used utilities** | Electricity, Gas, Compress air, Steam |
| **Production capacities** | 8 ton /day |
| **No. of chamber** | 3 |
| **Maximum fabris width** | 102” |
| **Minimum fabric witdth** | 30” |
| **Steam pressure** | 2 bar |
| **Air pressure** | 10 bar |
| **Applied for** | Open tube fabric |
| **No. of ratamatic burner** | 6 |
| **Extra Attachment** | Mahlo weft straightener |
| **M/C parts** | Burner,Nozzle, Exhaust air fan, Over feed roller, Suction fan, Chain arrangement |

## SANFORIZING/ANTI-SHRINKAGE FINISHING

### Sanforizing:

Sanforizing is a controlled compressive shrinkage process, which is applied on woven fabric to achieve shrinkage before making the garments. After sanforizing the residual shrinkage of woven fabric may be zero. In sanforizing process shrinkage is achieve by passing the cotton fabric onto a movable elastic felt blanket is released it assumes a shortened conditional. Thus the **cotton** fabric is forced to conform this compression.

***Residual Shrinkage:***

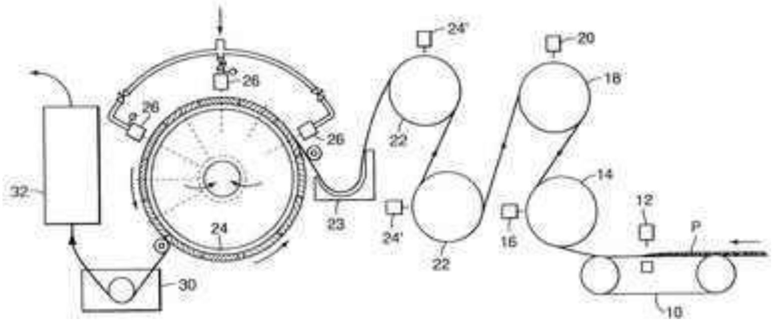
Residual Shrinkage is the latent shrinkage of a fiber ,Filament, yarn or fabric.

***The shrinkage amount of fabric is dependent on:***

1. The nature of fibers
2. The character of threads
3. The way of interlacing of thread in the fabric.
4. Crimp in yarn.
5. Cycle of washing no. of washing.

***Sanforizing Process:***

Sanforizing is a mechanical **finishing process** of treating textile fabrics to prevent the normal dimensional alternation of warp and weft. It is also called anti-shrinkage finishing process. It is a process of treatment used for cotton fabrics mainly and most textiles made from natural or chemical fibres, patented by Sanford Lockwood Cluett (1874–1968) in 1930. It is a method of stretching, shrinking and fixing the woven cloth in both length and width, before cutting and producing to reduce the shrinkage which would otherwise occur after washing .



Simplified diagram of the sanforizing method of producing shrinkage

Sanforizing process is based on the principle that when a elastic felt blanket is passed around a metal roller in contact with it, its outer surface is process extended and the inner surface contracted. So the process is called controlled compressive shrinkage process.

# MODULE – IV

# CHEMICAL FINISHING

# 4. CHEMICAL FINISHING

## 4.1 OBJECTS OF CHEMICAL FINISHING

- To change the surface characteristics of textile materials.
- To increase life and durability of textile materials.
- To set the chemicals into the textile materials.
- To impart new characteristics/properties of textile materials such as flame retardant, water repellent or water proof finishes.
- To meet up specific end uses.

## 4.21 CREASE RESISTANCE FINISH

### Introduction

Cellulose fibres and especially cotton are still the most important kind of fibres, because of their numerous advantages. One of their main disadvantages, wrinkling after washing is overcome by a very important and special kind of finish. It is difficult to find the one best term to describe this class of finishes. Some of the words and phrases that have been used in the past include easy care, minimum care, easy-to-iron, no-iron, wash and wear, crease resistant, durable press, permanent press, shrink proof, wrinkle resistant and wrinkle free.

Easy-care and durable press finishes are generally applied to cellulose andcellulose blend fabrics, but other fibres can benefit from these finishes also. Inaddition to the dimensional stability properties mentioned above, the sheen ofcalendered fabrics (permanent chintz) and the stand and hand of pile fabrics are generally improved by durable press finishes. The primary effects of the easy-care and durable press finish on cellulosic fibres are reduction in swelling and shrinkage, improved wet and dry wrinkle recovery, smoothness of appearance after drying, and retention of intentional creases and pleats.

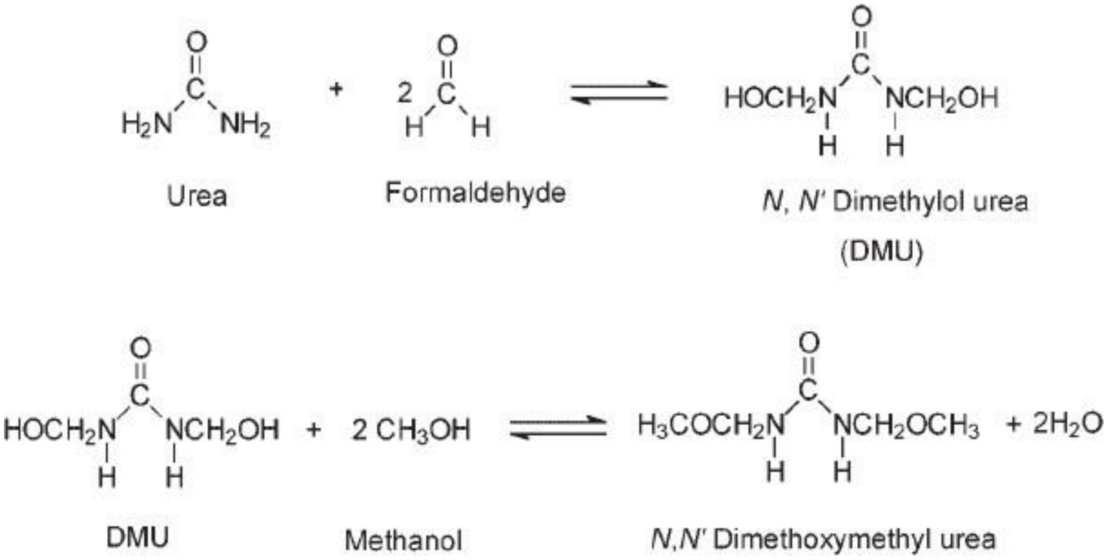
### Mechanisms of easy-care and durable press finishing

The primary cause of the shrinkage of cellulosic fibres is the fact that these fibres can readily absorb moisture. This absorbed moisture facilitates internal polymer chain movements in the amorphous fibre areas by lubrication. It disrupts the internal hydrogen bonding between these polymer chains. When a moisture laden cellulosic fibre is stressed, the internal polymer chains of the amorphous areas are free to move to relieve that stress. Hydrogen bonds can reform between the polymer chains in their shifted positions, in effect locking in the new configuration. With no restoring forces available, a newly formed wrinkle or crease will remain until additional processes (ironing for example) apply adequate moisture and mechanical forces to overcome the internal forces.

The swelling of cellulosic fibres by moisture can be reduced by the application of self crosslinking urea or melamine products as well as by products that mainly crosslink with cellulose molecules. Without such a crosslinking finish, cellulose fibres can take up more than 10 % of their weight in water. As the fibres swell, the fabric must crease and shrink to relieve the internal stresses caused by the swelling.

The new arrangement of the cellulose molecules in the swollen form of the fibre is fixed by newly formed hydrogen bonds between adjacent cellulose molecules, mostly in the amorphous fibre area. Therefore the uneven and wrinkled appearance of the cellulose fabric remains after drying, in contrast to fabrics made of nonswelling synthetic fibres.

Two different chemical approaches have been used commercially to produce non-swelling or durable press cellulose fabrics. The original approach is the incorporation of a polymerised finish in the pores of the fibres, so that water molecules cannot easily penetrate the fibre. The newer approach is the reaction of multifunctional crosslinking agents with the hydroxyl groups of adjacent cellulose molecules that hinder the swelling of the cellulose fibre.

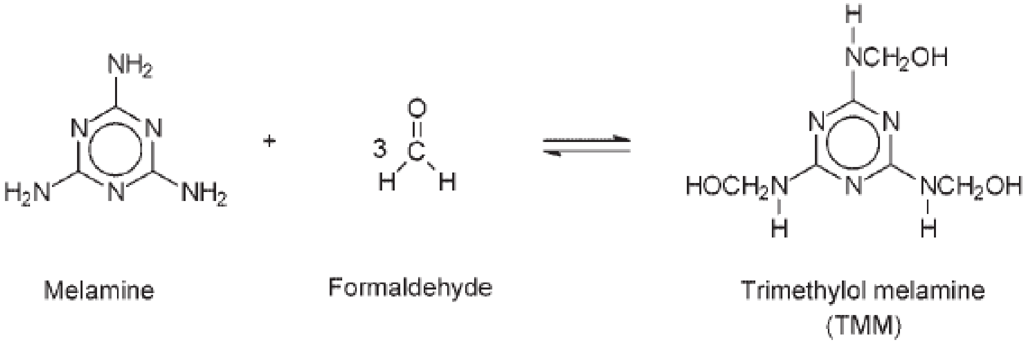


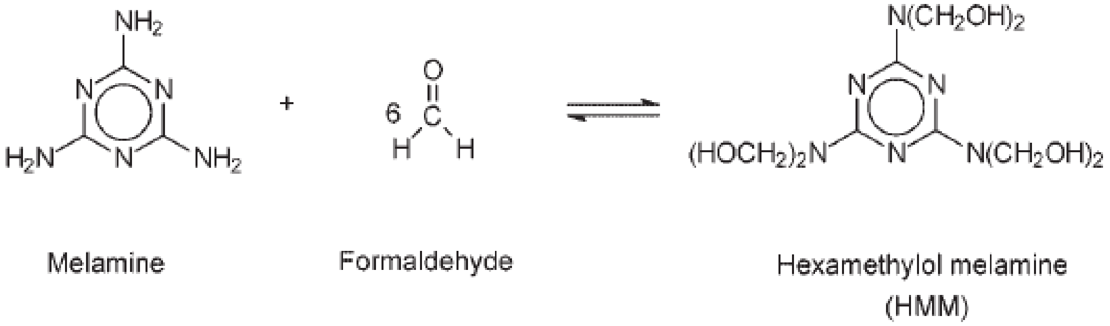
**Dimethylol Urea reaction**

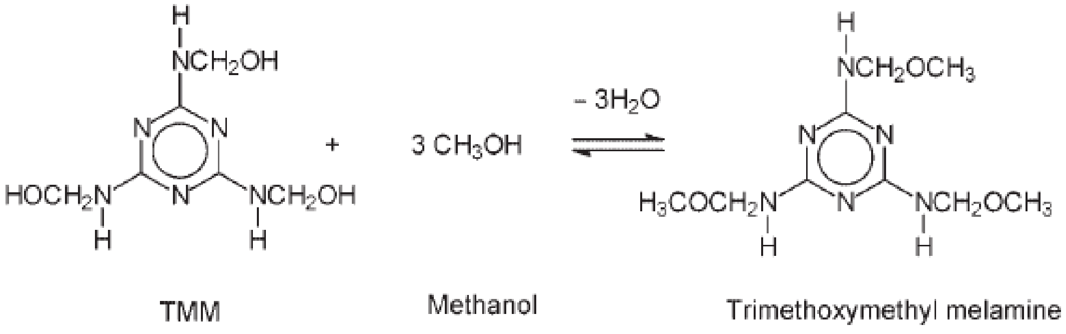
### Chemistry of easy-care and durable press finishes

### Formaldehyde-containing products

Urea–formaldehyde (U/F) products are readily synthesised from water solutions of urea and formaldehyde at pH 7.5–9. The resulting *N*,*N*′-dimethylol urea (DMU) is often modified by further reaction at pH 8–9 with methanol to the more stable and liquid dimethylether of DMU (dimethoxymethyl urea) as shown in **Fig**. These reactions are equilibrium reactions with significant concentrations of the starting compounds. These equilibria are the reasons for the high content of free and easily released formaldehyde found with U/F products. Because of their high reactivity, unmodified U/F finish baths must be used within a few hours. The high stiffness and firmness of the U/F finish can be important for rayon fabrics which often are considered too limp when compared with cotton. The U/F finish gives the best elastic resilience.







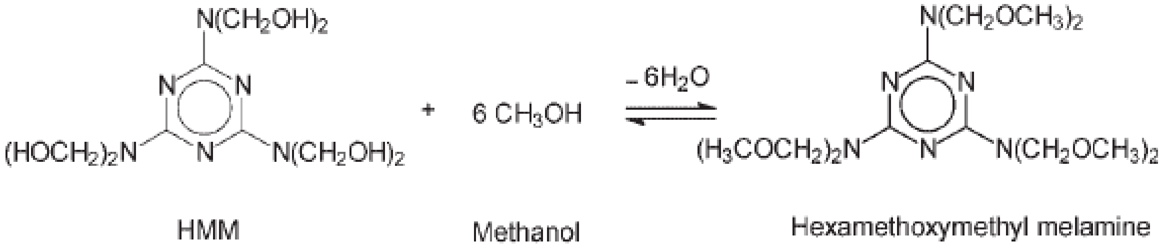


**Fig. Melamine formaldehyde reactions**

The main properties of U/F products are:

- DMU is highly reactive; finish baths have to be used in a few hours
- Low stability to hydrolysis, low durability to laundering
- High chlorine retention
- High content and release of formaldehyde
- Very high elastic resilience.

Melamine–formaldehyde (M/F) products have mostly three to six reactive *N*-methylol groups connected to one melamine ring. This leads to a higher crosslinking and an easy-care finish with better wash fastnesses. Their synthesis is similar to the U/F products, providing tri- to hexamethylol melamine (TMM, HMM) and their methyl ethers (tri- or hexamethoxymethyl melamine) as shown in **Fig.** TMM is preferred for the easy-care finish, often only as a component of a product mixture to give a better permanence of the effects. It is also used for permanent chintz (glazing, embossing, Schreinering) of cellulosics. HMM findsadditional uses in pigment binders and Basofil fibres.

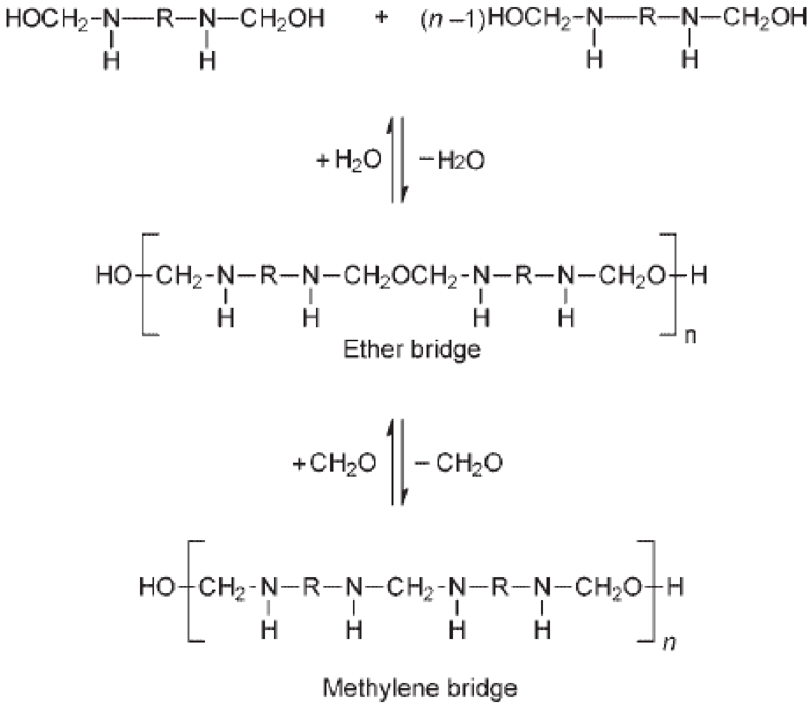
The main properties of M/F products are:

- Better stability to hydrolysis and better washing durability than U/F products
- Relatively high formaldehyde content and release
- Fewer problems with chlorine retention than U/F products
- More dimensional stability and stiffness (also for nylon and polyester).

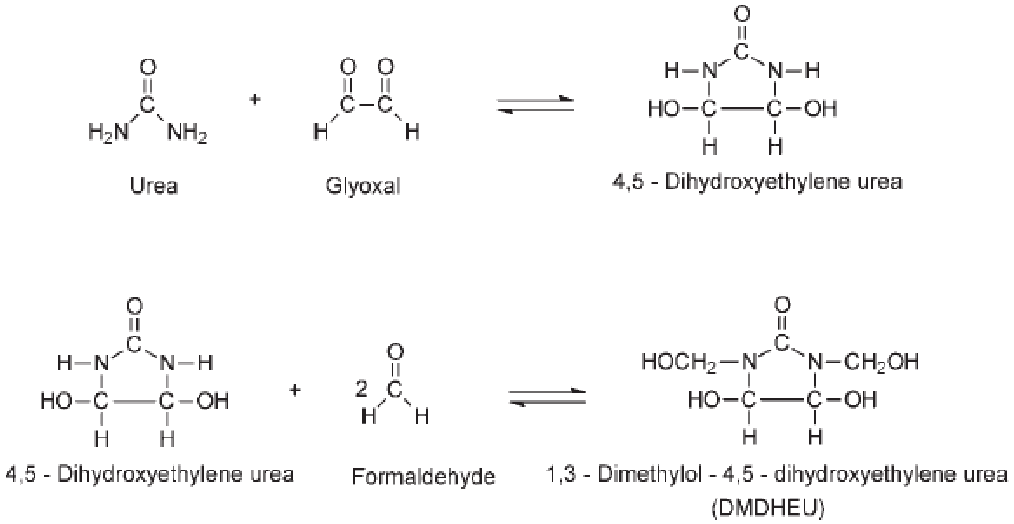
The predominant reaction of U/F and M/F products is their self condensation to three dimensional resin structures (**Fig**.). These structures impart a very stiff, firm handle to fabrics treated with U/F and M/F products. The self condensation is caused by the active hydrogen atom attached to the nitrogen of the *N*-methylol group. If this active hydrogen atom is substituted by a carbon atom in a ring structure, as in ethylene urea, the reaction with the hydroxyl groups of cellulose becomes dominant. Crosslinking of neighbouring cellulose molecules is then the main reaction, especially activated by inductive effects of the hydroxyl groups in the dihydroxyethylene urea heterocycle (DHEU).

*N*,*N'*-Dimethylol-4,5-dihydroxyethylene urea (DMDHEU) is the chemical basis of about 90 % of the easy-care and durable press finish products on the market. DMDHEU is synthesised from urea, glyoxal and formaldehyde as shown in **Fig.**

It is less reactive than DMU and TMM and therefore requires more active catalysts. However, finish baths containing DMDHEU are more stable than finish baths with DMU or TMM. The reactivity of DMDHEU can be further reduced by reaction with methanol or diethylene glycol, leading to ether- modified DMDHEU products. These alcohols are also formaldehyde scavengers and are often added to commercial finish products for that purpose. Diethylene glycol has the additional advantage of a high boiling temperature of 254 °C (490 °F). Therefore a significant portion can remain in the cured fabric and reduce the free formaldehyde content via acetal formation. Adddition of diethylene glycol also improves the chlorine fastness and the degree of whiteness.



Self condensation reactions of U/F and M/F products.



Synthesis of DMDHEU.

A typical DMDHEU commercial product is made from about 45 % DMDHEU, 9% diethylene glycol and 2% methanol. This product could contain less than 0.3 % free formaldehyde. As indicated there are two ways to incorporate diethylene glycol into these products. One version is a simple mixture of the glycol and DMDHEU. The other involves reacting the glycol with DMDHEU to form a glycolated product. Both products perform similarly and both types are available in the market place and are referred to as ‘ultra low formaldehyde’ (ULF) with less than 50 ppm released formaldehyde in the AATCC Testing Method 112-1983 .

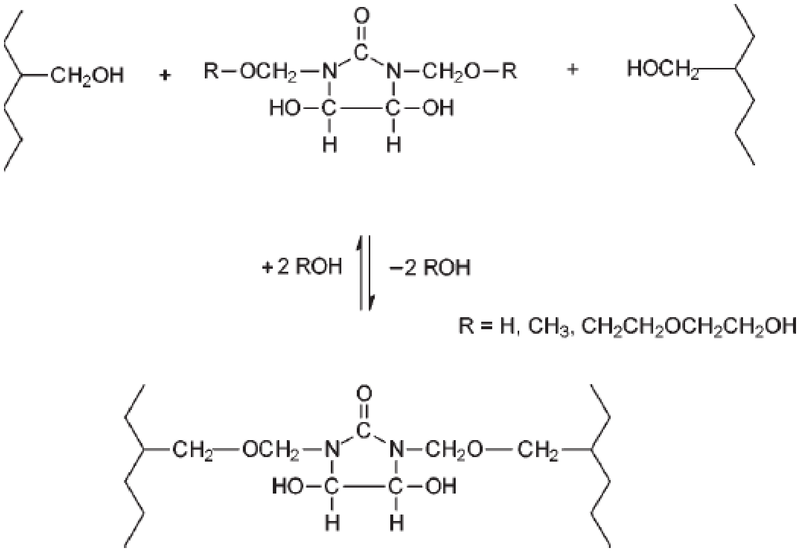
The principal reaction of DMDHEU products is the crosslinking of adjacent cellulose molecules, as shown in **Fig.** This crosslinking prevents the movement of the fibre molecules during stress and hinders shrinkage and wrinkle formation. This lack of molecular movement also leads to the fabric tensile strength and tear strength loss associated with durable press finishes because without crosslinking, the tear stresses can be distributed over many molecules which can slightly shift sharing the external forces.

The main properties of DMDHEU-based products are:

- Low to very low reactivity (when ether modified)
- Excellent durability to laundering
- Low chlorine retention
- Medium to very low formaldehyde release (Table 5.4)
- The most commonly used durable press products.

**Formaldehyde considerations**

There are several aspects to the ‘formaldehyde problem’. Formaldehyde is not only a very useful and inexpensive chemical compound but also a natural product. Traces of formaldehyde are present in air, fruits, vegetables, wood, and in blood. Every incomplete burning process, including cigarette smoking, produces formaldehyde. Formaldehyde does not build up in the environment because oxygen in the air reacts with it to form formic acid. More than 1 ppm of formaldehyde in the air causes a pungent odour (the threshold detection level by smell is 0.5 ppm). Formaldehyde irritates mucous membranes, causes teary eyes, induces cough, and can lead to difficulties in breathing and headaches. Skin contact with aqueous solutions of formaldehyde or with textiles that contain a high level of formaldehyde can give rise to eczema and occasional allergic reactions. In addition, formaldehyde is a suspected human carcinogen.

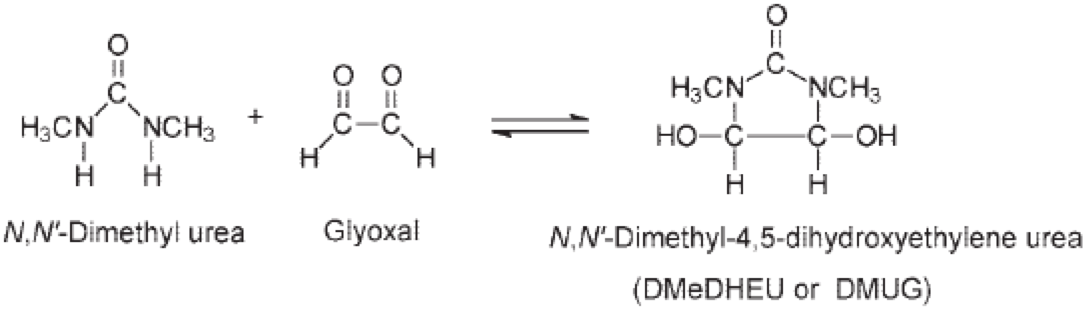


Crosslinking of cellulose with DMDHEU products.

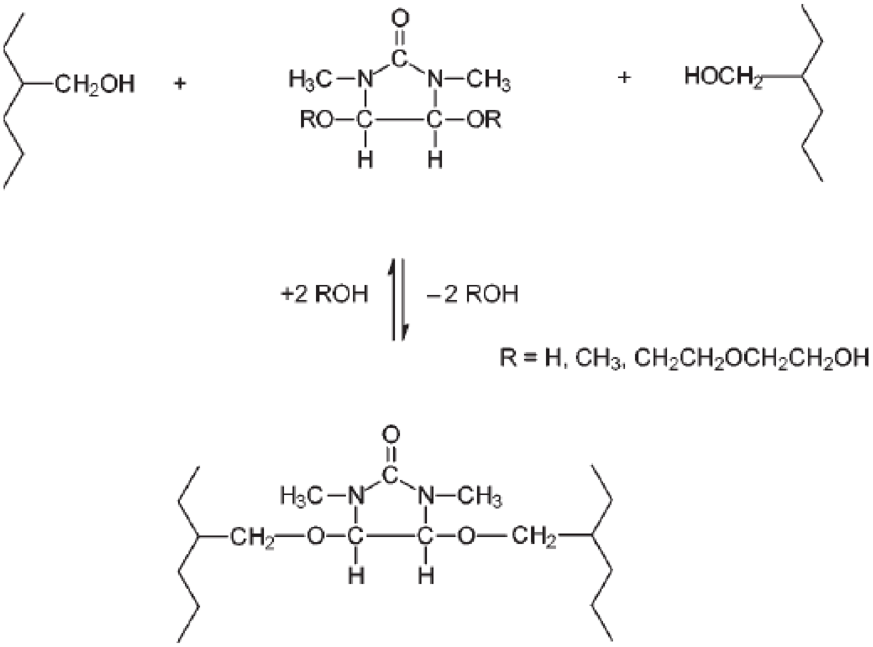
The most severe problems with formaldehyde and textiles occurred in the cut and sew industries before the introduction of DMDHEU. In normal usage, when clothing is periodically laundered, there are no formaldehyde-related problems. However, it is advisable to wash durable press treated textiles before their first use. Several countries have enacted laws designating concentration limits for formaldehyde in the workplace (0.75 ppm in the USA and 0.5 ppm in Germany). There are also governmental restrictions (for example European Community, Japan), company requirements (for example Levi Strauss, Marks and Spencer) and several labels (for example Öko-Tex Standard 100) that set limits for free or easily freed formaldehyde in textiles. These limits are always specified by a particular test method for formaldehyde because there are significant differences in results between the various formaldehyde test methods. For example, finished fabrics for adult clothing and other skin contact textiles may be labelled and called low formaldehyde finished according to Öko-Tex Standard 100 when their free formaldehyde content is lower than 75 ppm according to the Japan Law 112 method.

## Non-formaldehyde containing products

*N*,*N*'-Dimethyl- 4,5-dihydroxyethylene urea (DMeDHEU) should not be confused with DMDHEU. DMeDHEU does not contain formaldehyde.



**Synthesis of DMeDHEU**



**Crosslinking of cellulose with DMeDHEU**

It is synthesized from the relatively expensive *N*,*N*'-dimethyl urea and gloxal (**Fig.**) and is often referred to as DMUG (dimethylurea glyoxalate) or DHDMI, derived from the name dihydroxy dimethyl-2-imidazolidinone. Like DMDHEU, it can be modified by reaction with alcohols such as methanol, diethylene glycol or 1,6-hexanediol to ether derivatives. The crosslinking reaction with cellulose is shown in **Fig.** The two hydroxyl groups in the 4,5-position of DMeDHEU are less reactive than the

*N*,*N'*-methylol groups of DMDHEU. Stronger catalysts or harsher reaction conditions are needed for successful crosslinking. DMeDHEU costs about twice as much as DMDHEU and in order to achieve comparable easy-care and durable press effects to DMDHEU, nearly twice the amount of DMeDHEU is needed.

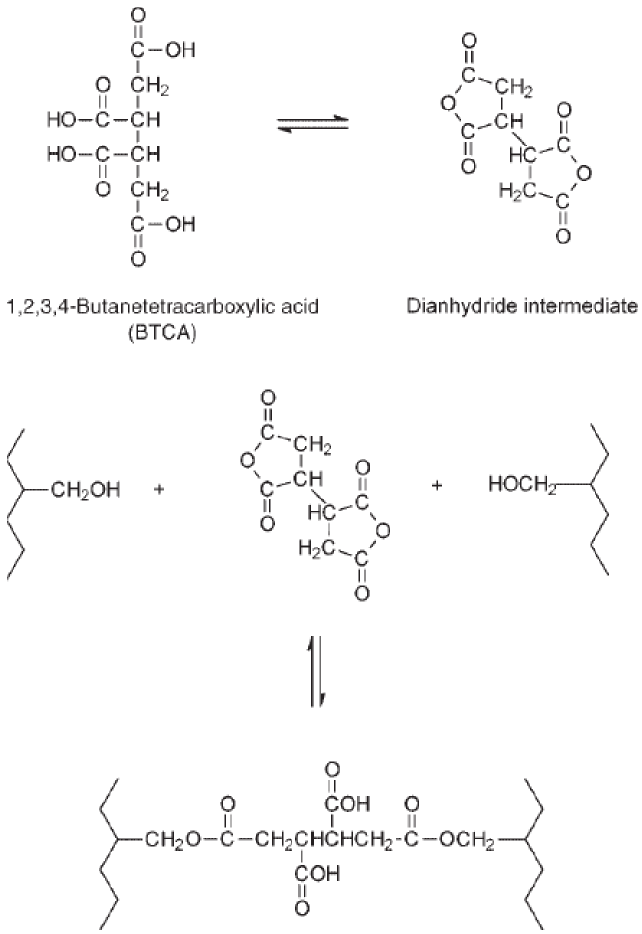
This poor cost performance ratio is one reason for the relatively small market penetration by this formaldehyde-free finish. Another reason is that a completelyformaldehyde-free finish is not as commercially important since the advent of the ultra low formaldehyde products. However, a 1:1 mixture of DMDHEU and DMeDHEU is popular because of its reduced formaldehyde levels with only slightly inferior physical properties at an acceptable cost.

The main properties of DMeDHEU products are:

- Formaldehyde free
- Very low reactivity
- Very low chlorine retention
- Limited durability to laundering
- Yellowing effect when not ether modified
- Price/effect ratio nearly 4:1 compared with DMDHEU
- Development of unpleasant odours, depending on the product formulation.

1,2,3,4-Butanetetracarboxylic acid (BTCA) and similar polycarboxylic acids provide an alternative possibility for a formaldehyde-free crease resistant finish. The activation mechanism of BTCA and the reaction with cellulose are shown in Fig. BTCA gives rise to good crease recovery but with limited laundering durability owing to hydrolysis of the ester bonds to cellulose. These polycarboxylic acids are relatively expensive, comparable in cost to DMeDHEU. In addition, the reactions of these acids with cellulose require large amounts of sodium hypophosphite as a catalyst. Not only is sodium hypophosphite expensive, but it is also a reducing agent that discolours certain dyestuffs, especially some reactive and sulfur dyes. Recently, polyacrylic acid-based products, for example maleic acid anhydride copolymers,16 have been introduced that provide similar properties to BTCA finishes but at a more economical price.

Novel cellulosic crosslinking agents with interesting properties are gained by molecular incorporation of the phosphorus catalyst in the BTCA structure. These formaldehyde-free phosphono- and phosphinocarboxylic acids (APCM, modified polycarboxylic acids) show good crosslinking properties with minimal strength losses, no shade changes and good durability for up to 20 washing cycles. The APCM products are liquid, water soluble and neither toxic nor skin irritating.



**Cross linking of cellulose with BTCA**

## Catalysts for easy-care and durable press finishes

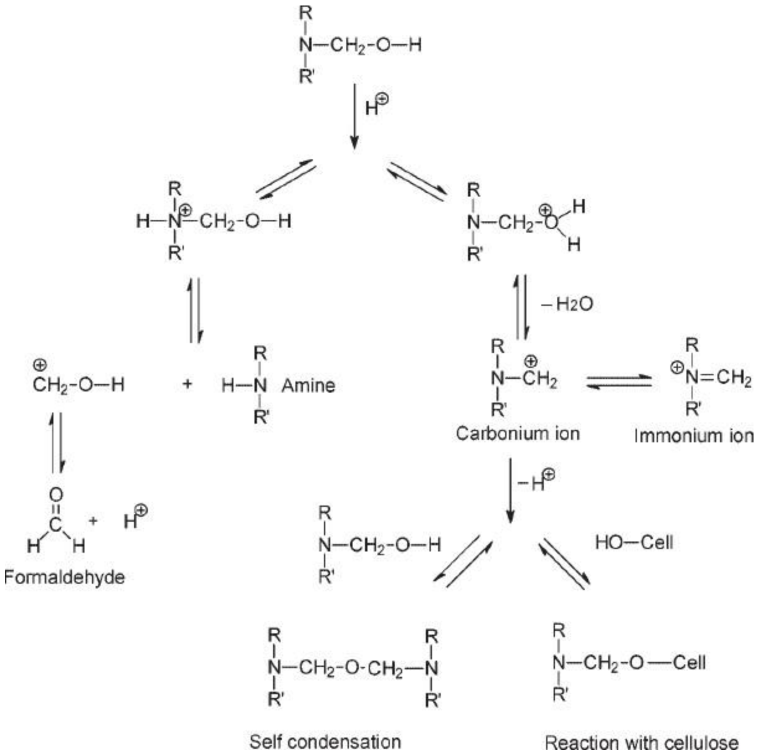
The reaction of *N*-methylol reactants such as DMDHEU with cellulose requires an acid catalyst for acceptable yields under conditions suitable for textile processing, for example, 150 °C (300 °F) to 170 °C (340 °F) for 0.5 to 3 min:

$$\mathbf{M2+ + 2\ H2O\ M\ (OH)\ 2 + 2H+}$$

## Application methods

The most common application method for easy-care and durable press finishes is a pad–dry–cure procedure. In this process, the crosslinking reactant, catalyst, softener, and other components are dried on the fabric prior to the crosslinking reaction that takes place during the curing step. If the finish is cured immediately after drying, while the fabric is still in an open width configuration, the finish is referred to as a ‘pre-cure’ finish, the finish is cured *prior* to garment manufacture.

Textiles with a pre-cure finish are most suited for fabrics and apparel that require wrinkle resistance, such as sheeting, shirting and casual trousers. For fabrics that require crease retention, such as trousers and pleated skirts, the durable press finish is only dried by the fabric manufacturer and cured after the garment has been made and creased appropriately. This finish is referred to a ‘postcure’ finish or ‘delay cure’ finish, the finish is cured *after* the garment has been manufactured.



***N*-Methylol reaction scheme.**

In the special cases where entire garments are to be treated with a durable press finish, the finishing chemicals can be sprayed in exact doses onto the garments before the final shape is formed and then cured. Also impregnation by dipping (garment dipping) or in a tumbler, followed by centrifugation, drying and pressing or ironing is common. The made-up garments are finally suspended on hangers in a curing oven.

## WATER PROOF FINISH

### Waterproofing:

“Waterproofing is nothing but preventing the passage of both air and water through a fabric.”

**Purpose of Water Proofing:**

For certain uses such as Tarpaulin, Umbrella cloth, Rain coat fabrics etc., it is required to give this type of finish as these type of fabrics are generally used against the air and water in the normal life. So they should have some property to prevent both air and water passing through them.

This finish makes the wearer feel uneasy and uncomfortable as the air circulation is not there.

Water proof fabric

**Principle of Water Proofing:**

A film on the surface of the fabric should be formed for the prevention of air and water.

When a uniform coating of suitable substances such as rubber is produced on the surface of a fabric, the interstices between the warp and weft yarns are blocked by the continuous film or substance and both water and air not pass through the treated fabrics.

It is a chemical and property giving finish.

**Requirements:**

The fabric should not become unnecessarily stiff and the fabric should have soil release or soil repellent property.

The finish should not alter the **fastness properties** or dyed material, feel, strength etc., of the fabric.

**Method:**

By two methods it can be carried out:

1. Methods by which hydrophobic substances are deposited on the cloth.
2. Methods by which the fabric itself becomes hydrophobic.

**Chemicals Used:**

1. Vulcanized natural rubber.
2. Oxidised oils of varnishes.
3. Polyvinyl chloro acetate.
4. Polyvinylidine chloride.
5. Cellulose acetate.
6. Cupprammonium hydroxide solution.

**Process:**

**A.** The simplest method of water proofing is the coating of fabric with rubber as a thin film.

**Disadvantage:**

- Unwanted stiffness and harshness.
- Fabric becomes harsh and brittle.

**B.** The application of natural oil will also produce this finish.

**Advantage:**

- No cracks or brittleness.

**Disadvantage:**

- It is not permanent.

**C.** Coating of water impermeable substances like pitch, asphalt and molten waxes produce water proofing.

**Advantage:**

- It will give excellent proofing.

**Disadvantage:**

- Many desirable properties of the fabric will be destroyed.

**D.** Using synthetic resins we can produce this finish.

Example: Polyvinyl chloro acetate, Cellulose acetate, Polyvinylidine chloride.

**E.** Water proofing with wax emulsion.

- It can be applied on cotton, linen, wool, silk fabrics.
- Aluminium acetate is used along with the wax emulsion.

There are two steps involved in producing this finish.

**1st step:**

Wax emulsion: 1-3 kg
Water : 50 litres
Pad the material with wax emulsion solution.

**2nd step:**

In wet condition,
Aluminium acetate: 1- 3 kg (12˚ Tw)
Water : 50 litres

Impregnate the fabric and squeeze thoroughly.
Then dry the fabric in a stenter or on a drying range at 110˚ to 120˚C.

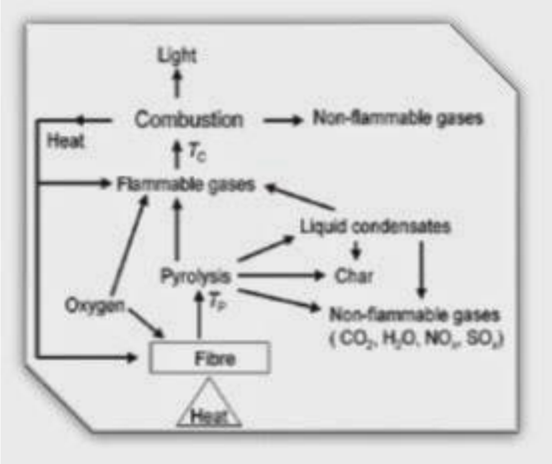
## FLAME RETARDANT FINISH

### Flame Retardants Finishes

Flame-retardant **finishes** provide textiles with an important performance characteristic.

- Protection of consumers from unsafe apparel
- Firefighters and emergency personnel require protection
- Floor coverings, upholstery and drapery protection
- The military
- The airline industry

## Mechanisms of Flame Retardancy



**Combustion:** is an exothermic process that requires three components,

- Heat
- Oxygen
- Suitable fuel.

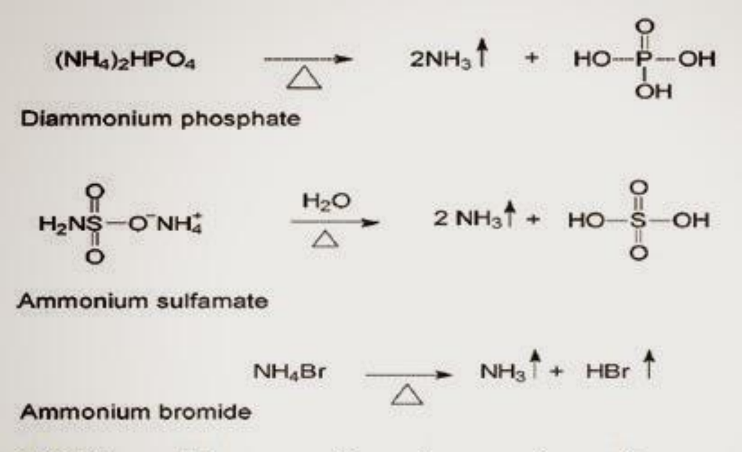
## Flame-retardant Chemistry

The synergistic effect of antimony comes from the volatility of antimony trihalides and the effectiveness of antimony compounds in scavenging free radicals over a broad temperature range (for example 245–565 °C).

## Flame Retardants for Cellulose Non

**durable:**

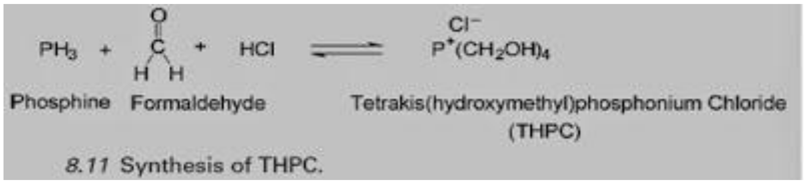
1. Inorganic salts have long been known to provide flame retardancy on cellulosic material that will not be exposed to water, rain or perspiration.
2. The French chemist Gay-Lussac proposed a borax and ammonium sulfate treatment as a flame retardant for cotton in 1820.
3. Today, a mixture of boric acid and borax is still an effective flame retardant for cotton at ~ 10 % solids add-on.
4. Ammonium salts of strong acids, especially phosphoric acid (P/N synergism) are particularly useful as nondurable flame retardants for cellulose. Example:



*8.10* Thermal decomposition of ammonium salts.

**Durable:**

1. The most successful durable flame retardants for cellulose are based on
    - Phosphorous- and nitrogen-containing chemical systems .
    - That can react with the fibre or form crosslinked structures on the fibre.
2. The key ingredient of one of these finishes is
    - Tetrakis(hydroxymethyl)phosphonium chloride (THPC),
    - Made from phosphine, formaldehyde and hydrochloric acid



*8.11* Synthesis of THPC.

## CARBONIZATION OF WOOL

### Wool Carbonizing Process:

Carbonizing is done to remove the cellulosic impurities from **wool** by treatment with acid or acid producing salts. Carbonizing may be carried out in loose wool or on piece goods after scouring. However, it is common practice to carbonise worsted piece goods as well as woolens. The process begins by immersing the wool in a solution of sulfuric acid (H2SO4) that reacts with the cellulose impurities in the wool.

**Fig: Carbonizing process of wool**

### Techniques of Carbonizing:

The conventional carbonizing process comprises five main stages : **scouring**, acidizing, drying and baking, burr crushing and dedusting and neutralising. And recent development process includes: Acidising, Moisture removal, Drying/Baking, Burr crushing and dedusting, Neutralisation.

**Fig: Carbonized wool**

### The conventional technique of wool carbonizing has the following basic steps:

1. Scouring of the raw wool with non-ionic detergent.
2. Rinsing.

3. Immersion in a long bowl containing 5-7% (w/v) sulphuric acid, 1-2 g/L detergent at 20-30oC.
4. Double squeezing and/or continuous centrifuging prior to drying.
5. Drying at 60-80oC to a low regain.
6. Baking at 95-120oC to carbonise the VM.
7. Pass through heavy fluted rollers to crush the embrittled VM.
8. Convey to a rotating shaker/de-duster to remove the charred VM dust.
9. Pass through a neutralising bowl usually containing sodium carbonate.
10. Rinsing with a small addition of detergent.
11. Bleaching wool with hydrogen peroxide at approximately pH 5 with formic acid.
12. Final drying.

The production rate through the process is usually low, typically 500-600 kg/h for an 1800 mm wide line, since sufficient time must elapse for the VM to adsorb the acid from the bowl and for subsequent baking to embrittle the acidified cellulose.

Wool piece goods are treated with sulphuric acid (6-8 o Tw) containing acid stable wetting agent and hydroextracted. The treated wool substance is dried at low temperature (60-70~ very quickly to minimise degradation by sulphuric acid of intermediate critical concentration. The dried wool is then heated at 110~ for a short time. The goods are then neutralised immediately or run dry through a dolly or milling machine to remove the charred vegetable matter and then neutralised.

Neutralisation of wool fabric can also be carried out in open-width scouring machine. Neutralisation with ammonia or ammonia/ammonium acetate mixtures removes acid from the fabric far more rapidly than either sodium carbonate and sodium acetate.

In a rapid carbonising process wool is treated in up to 8% (w/v) sulphuric acid solution for 30 sec and time delay of about 10-15 min is introduced before drying. The locally damaged areas can greatly weaken the fibre if surface acid is not evenly distributed during drying. However, in the rapid carbonising method and total acid inside the wool changes. Free surface acid penetrate into the wool fibres and bonds to wool. Thus the amount of concentrated acid formed during drying and baking is minimised and as a consequence, less chemical attack occurs to wool in rapid carbonising.

Magnesium chloride, aluminium chloride (8-10 ~ Tw) or gaseous hydrochloric acid may also be used for carbonising of wool. Rags are carbonised to remove cotton stitchings prior to use in shaddy by the 'dry carbonising' process by exposing to hydrochloric acid gas in an enclosed chamber. Metal acid salts liberate hydrochloric acid at high temperature and attack the cellulose in wool. But owing to their high cost and higher temperatures required which cause injury to dry wool, are rarely used.
The wool burrs contain hemi-cellulose and lignin apart from cellulose. The lignin is not effected by carbonising process on acid hydrolysis, but can be split oxidatively. Salt ofpersulphuric acid accelerates degradation of wool burrs which enable shortening the time of reaction.

Natural soiling of wool and vegetable matter and skin flakes, can also be enzymatically modified. The replacement ofcarbonisation by the use of enzymes, such as cellulases, ligninases, hydrolases, lyases, oxidoredulases etc. are reported. The main advantages of enzymatic carbonizing are reduced wool fibre damage, effluent load and energy consumption.

Carbonised wool are more porous than scoured wool and hence the dye uptake is higher. Uneven dyeing may result due to faulty carbonising.

## MOTH PROOF FINISH ON WOOL

### Moth Proofing:

“Moth proofing is a finishing which is given to prevent the growth of moth.” It is one kind of special **finishing process** of textile.

It is a chemical and property giving finish.

### Purpose of Moth Proofing:

It is mainly carried out on wool fabrics as the keratin molecules are consumed by moths as food.

Since woolen fabrics are costlier, they have to be protected from moth.

Moth is a small insect that feeds on substances like keratin and fibroin and so animal fibres are more susceptible to the attack of moth.

Moth proof finished bag

Woolen and worsted materials are attacked by moth and quickly eaten away and the housewives have to be very careful in preserving such garments.

**Requirements:**

The finish should not affect the strength, drape, handle, softness, **fastness property** of dyed fabric and it should not cause any irritation to the human skin.

The finish should be fast to wash, light and laundering.

**Process of Moth Proofing**

Moth proofing can be done in the following ways:

1. By exposing the material to sunlight or sulphur-di-oxide.
2. Using Naphthalene balls and para dichloro benzene.
3. Using some substances containing fluorine such as Sodium fluoride, Aluminium fluoride, Potassium fluoride, and Sodium antimony fluoride.
4. Using soluble solvents such as Dichloro Beneze, Sulphomethylamid and Dichloro Trichloro ethane.
5. Evlan-BL and Mittin FF also produce moth proofing. These are the bet mothicides.

**Process Sequence:**

Pad-dry-cure

Concentration-20% on the weight of the material.

**STONE WASH ON DENIM FABRIC**

**Stone wash:**

For bringing fading effect on denim stone wash is done. Stone wash also helps to increase the softness and flexibility of otherwise stiff and rigid fabrics such as canvas and **denim**. This process could result in colour-fading of jeans and there is added usage of water for the **washing**.

**Figure-1: Stone washed jeans**

Volcanic rocks or pumice stones (Figure-2) are added during washing as abradants. The colour fading is more apparent but less uniform. The degree of colour fading depends on the washing time (60–120 min), stone ratio (weight of stones relative to weight of the garment) (0.5: 1–3:1), size of stones (diameter: 1–7 cm), liquor ratio (∼10:1) and garment load. The world's major pumice stone supplying countries include the USA, Turkey, Italy, Germany, Iceland, New Zealand, Japan, Indonesia and Philippines.

## Flow Chart of Stone Wash:

Stone washing process flow chart for any garments is in the following-

Garments loading with stone
↓
De-size
↓
Rinse (Two times)
↓
Stone wash
↓
Rinse (Two times)
↓
Softener

↓

Unload the garments

↓

Extracting

↓

Drying

Stone washing of denim fabric gives ‘used’ or ‘vintage’ look on the garments. This is due to the varying degree of abrasion in the garment. Traditionally, stone washing of denim garments is carried out with pumice stones to achieve a soft hand and desirable look. The pumice stones having an oval and round shape with a rough surface work as an abradant in washing cycle. The variations in shape, composition, hardness and porosity result in different washing effects in the **denim fabric**. During washing, these stones scrape off dye particles from the surface of the yarn of the denim fabric which shows a faded, worn out and brilliance effect in the denim fabric. From ring dyeing of denim fabric and heavy abrasion during stone washing, the fading is more apparent but less uniform. Stone washing makes the denim garments more supple so that they fit comfortably. To get the desired washed effect, the stone should be of proper hardness, shape and size. For heavy weight denim fabric, large and hard stones are suitable and also last longer. Similarly, smaller and softer stones are suitable for lightweight denim fabrics

**Figure-2: Pumice stones**

**Procedure of Stone Wash:**

The procedure is as follows:

1. Load stones into the machine.
2. Load garments into the machine (the ratio is usually 0.5–3.0 part weight stones to 1 part weight garments).
3. Desize with α-amylase enzyme and detergent. The liquor ratio is approximately 5–8:1.
4. Rinse.
5. Refill and tumble with stones for 30–90 min, depending on the desired effect. The Liquor ratio is 5–8:1 at 50–70°C. Scouring additives can also be used.
6. Drain. Separate garments from stones (garments can be transferred to another machine).
7. Rinse.
8. Apply a softener (garments can be transferred to another machine for softening).
9. Extract and unload.
10. Destone and tumble dry.
11. Press, if required.

Softeners and/or lubricants can be added during Steps 3 and 5 to reduce the potential for creasing.

**Effect of stone ratio:**

Figure-3 shows that with stone ratio below 0.5:1, no significant colour fading effect in the denim garments is noted. When the stone ratio is high, the colour fading effect becomes enhanced. However, too high a stone ratio may cause severe abrasion leading to fabric damage.

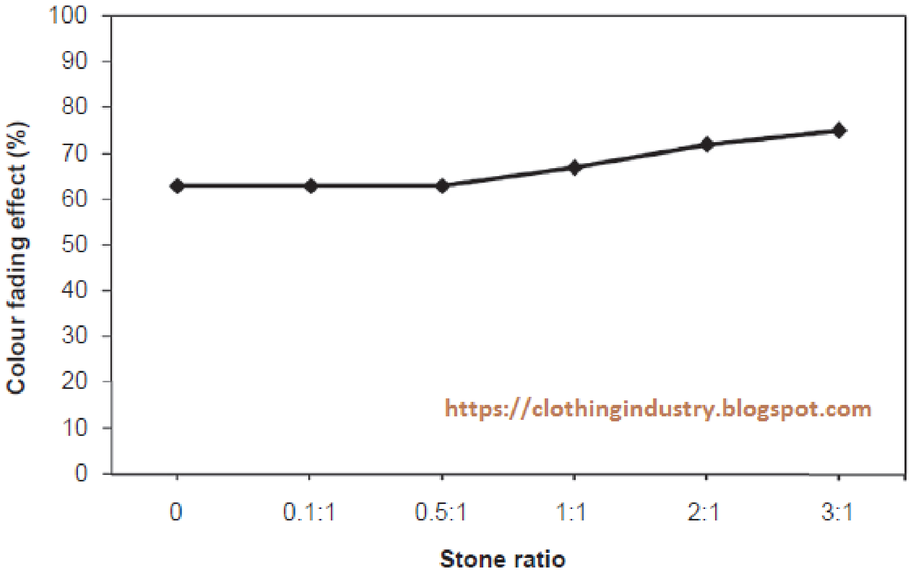


**Figure-3: Effect of stone ratio on the colour fading effect.**

A: diameter = 2.0–3.5 cm; B: diameter = 3.6–5.0 cm; C: diameter = 5.1–6.5 cm; D: diameter = 5.5–7.0 cm.

**Effect of stone size:**

Figure-4 shows the effect of stone size on the colour fading effect. It is noted that the smaller the stone size, the better is the colour fading effect. In addition, small stones can provide an even and uniform abrasion effect, but the colour contrast produced is not good when compared with large stones.

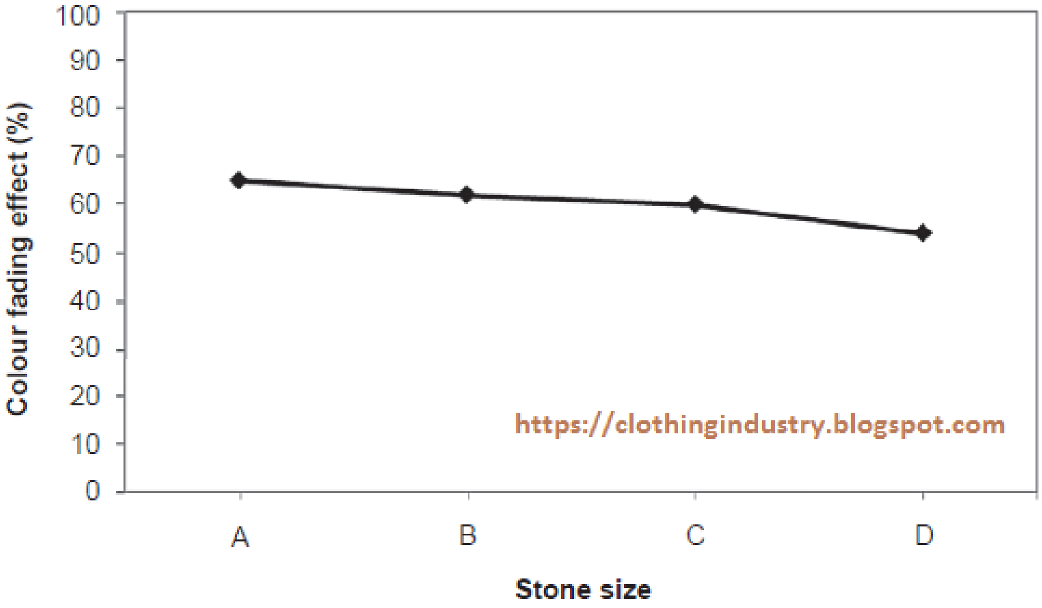


**Figure-4: Effect of stone size on the colour fading effect**

A: diameter = 2.0–3.5 cm; B: diameter = 3.6–5.0 cm; C: diameter = 5.1–6.5 cm; D: diameter = 5.5–7.0 cm.

**Effect of stone washing time:**

Figure-5 shows the colour fading effect under the influence of stone washing time. It is shown that after 90 min, there is no further increase in the colour fading in denim garments.

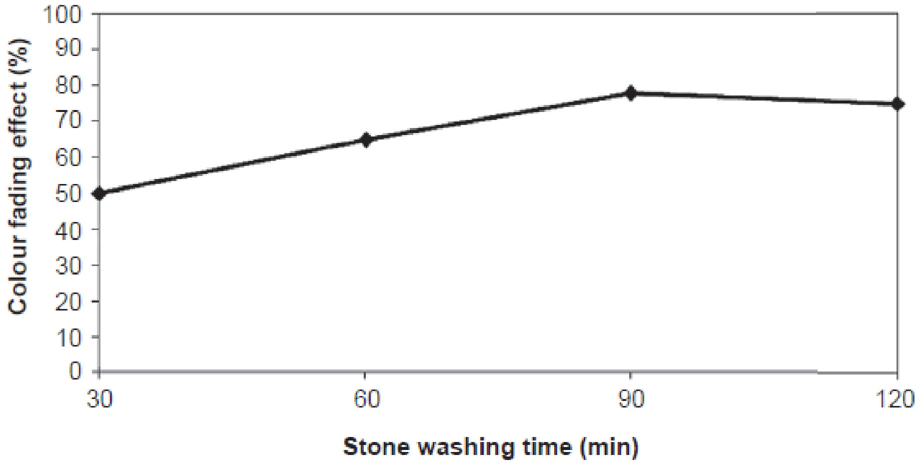


Figure-5: Effect of stone washing time on the colour fading effect

**Stone washing of denim fabric with pumice stones has some disadvantages and limitations, such as:**

1. Stones may cause wear and tear of the fabric and may damage the washing machine from abrasion of the stone with fabric or machinery parts.
2. It may also create the problem of environmental disposition of waste of the grit produced by the stones.
3. Increase the labour cost required to remove stone dust from finished garments. **Denim garments** are required to be washed several times for complete removal of the stones.
4. The stone washing process may cause back staining and redeposition.
5. The process is non selective.
6. Metal buttons and rivets in the garments as well as the drum of the washing machine sometimes get abraded which substantially reduces the quality of the garment and the life of the equipment.

## MERCERIZATION

| | |
|---|---|
| ➔ | 1844 - John mercer observed the effect. |
| ➔ | 1850 – Filed a patent for treatment of cotton with concen. NaOH solution with improvement in strength & dyeability. |
| ➔ | 1890 – Horace Lowe; found if shrinkage is controlled, the fabric becomes lustrous. |
| ➔ | Tension Mercerization (Lowe) & Slack Mercerization (Mercer) |

**Mercerization is carried out for the following purpose.**

1. Improving lustre (silky look, in tension mercerization only).
2. Improving tensile strength.
3. Improved dimensional stability.
4. Increasing uniformity of dyeing & improving color yield (savings in dyestuff).
5. Improving Elasticity or Stretch material (in slack mercerization only).

**Mercerization is a process of impregnating the textile material with a concentrated solution of cold NaOH, keeping it in contact with this cold solution for a given time with or without tension, and subsequently rinsing it.**

**MECHANISM-**

- Mercerization causes swelling in fibre
- Swelling causes Cross-section to become rounder, loss of convolutions & detwisting leading to more lustrous surface
- Opening of fibre structure
- Increase in amorphous content due to decrystallization
- Although mercerization is accompanied by swelling, it is more closely related to internal modification of fiber.
- Effect is observed at 18-24 % w/w NaOH solutions.
- Higher no of –OH groups available as compared to un-mercerized cotton
- Higher moisture regain, dye-uptake and reactivity

**The effect of mercerization is related to the size of the sodium hydroxide hydrates ($NaOH. xH_2O$). The concentration of NaOH solution determines the value of x or the size of the hydrate. A dilute solution has larger sized hydrates, which can cause swelling in cotton fibre by entering the amorphous phase of the fibre. At higher concentrations, the hydrate volume is smaller. Such hydrates cause lower swelling but have the ability to penetrate the crystalline phase and change the**

**crystal structure. Such changes are capable of inducing important structural modifications in fibre structure.**

**In the table given below, the composition of NaOH hydrate, corresponding NaOH concentration and the type of hydrate formation are shown:**

**Sodium Hydroxide Hydrates: Composition, Type and Concentration of Maximum Frequency**

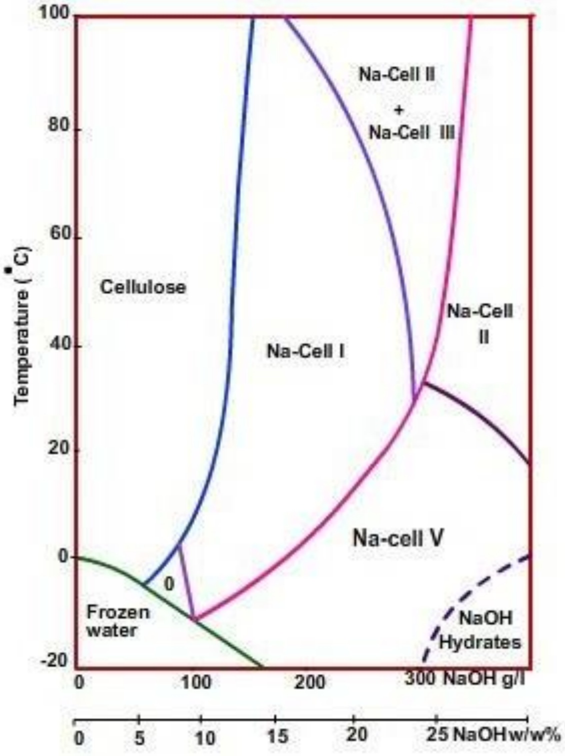
| **Composition of hydrate** | **NaOH Conc. (% by Wt.)** | **Type of hydrate** |
|---|---|---|
| $NaOH.20H_2O$ | 6-9 | Hydrated ion pair |
| $NaOH.12H_2O$ | 13.5-15 | Hydrated ion pair |
| $NaOH.10H_2O$ | 18 | Solvated dipole hydrate |
| $NaOH.H_2O$ | 69 | Dipole hydrate |
| $NaOH.7H_2O$ | 22.8-24.1 | Solvated Dipole hydrate + D.H. (7.4 A°) |
| $NaOH.5H_2O$ | 30.2-30.9 | Dipole hydrate |
| $NaOH.4H_2O$ | 34.8-35 | Dipole hydrate |
| $NaOH.3.5H_2O$ | 38-38.8 | Dipole hydrate |
| $NaOH.3.1H_2O$ | 41.8-42.6 | Dipole hydrate (Dia 6 A°) |
| $NaOH.2H_2O$ | 52.6 | Dipole hydrate |

**In the table given below, the variation in the hydrodynamic volume with changing hydrate type is given.**

| **Composition of hydrate** | **Hydrodynamic volume (dia Å)** |
|---|---|
| Dipole Hydrate | 5-8 |
| Solvated dipole hydrate | 8-10 |
| Hydrated ion pair | 10-15 |
| Separated Hydrated ion pair | 15-20 |

**When a sodium hydroxide solution of a given concentration is used for treatment of a cellulosic fabric (cotton), it forms a ternary complex, the composition of which is governed by the concentration of NaOH solution. This complex is known as soda cellulose. These soda celluloses have well defined crystalline character which is verified from their x-ray diffraction patterns.**

**Given below is the phase diagram of soda celluloses.**



**Phase diagram of soda celluloses**

In the figure given above, it can be seen that soda celluloses of defined x-ray diffraction pattern are formed on treatment with NaOH solutions of different concentrations at different temperatures. Although it seems that there are well defined boundaries for formation of various soda celluloses, in reality it is not the case.

Na-Cell I forms when cotton or ramie is treated with 12-19% (w/w) NaOH solutions at 20°C. Decomposition of Na-Cell I leads to cellulose II formation. At higher concentrations, Na-Cell II is formed. Drying of Na-Cell I results in formation of Na-Cell III.

Washing of Na-Cell I and II results in formation of Na-Cell IV. In fact, Na-Cell IV is only a cellulose hydrate as washing removes the alkali and decomposes the ternary complex. In a way it is a swollen form of cellulose.

At low temperatures, Na-Cell V is formed. During washing of Na-Cell V, Na-Cell IV is formed first and then Cellulose II is formed.

In the table given below, composition of Na-Celluloses and corresponding hydrates is given.

Soda Celluloses: Composition and corresponding sodium Hydroxide hydrate

| **Soda celulose type** | **Comoposition** | **Corresponding hydrate** |
|---|---|---|
| Na-Cell I | $C_6H_{10}O_5$ , NaOH, $3H_2O$<br>$(C_6H_{10}O_5)_2$ , NaOH. $2H_2O$<br>$(C_6H_{10}O_5)_2$ , NaOH. $1.5H_2O$ | NaOH. $5H_2O$<br>NaOH. $7H_2O$<br>NaOH. $10H_2O$<br>NaOH. $12H_2O$ |
| Na-Cell II | $C_6H_{10}O_5$ , NaOH. $H_2O$ | NaOH. 3-$3.5H_2O$<br>NaOH. $2H_2O$ |
| Na-Cell III | $C_6H_{10}O_5$ , NaOH. $2H_2O$ | NaOH. $4H_2O$ |
| Na-Cell IV (Q) | $C_6H_{10}O_5$ , $H_2O$<br>$C_6H_{10}O_5$ , 0-0.3NaOH. $H_2O$<br>$C_6H_{10}O_5$ , 1.3 or 1.5NaOH. $2H_2O$ | NaOH. $20H_2O$<br>NaOH. $12H_2O$ |
| Na-Cell V | $C_6H_{10}O_5$ , NaOH. 4-$5H_2O$ | NaOH. $5H_2O$<br>NaOH. $7H_2O$ |

## What are Cellulose I and Cellulose II?

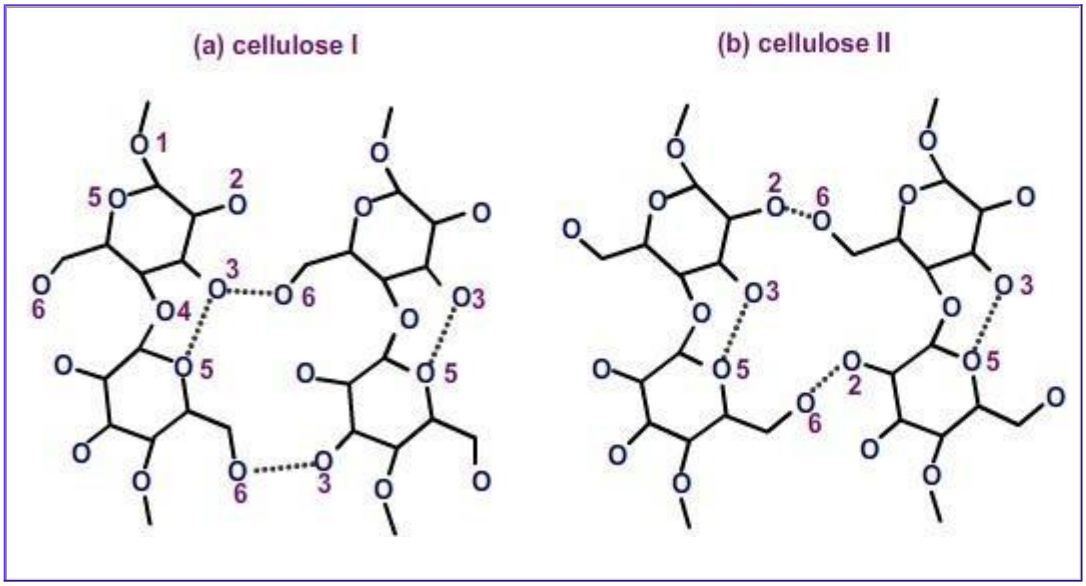
The native form of cellulose which occurs in cotton and other natural cellulosic fibres, is known as cellulose I. It has it unique crystal diffraction pattern (monoclinic). It is a thermodynamically less stable form of cellulose. When cellulose in converted to regenerated cellulosic fibres like viscose, dissolution of cellulose is an intermediate step. During regeneration, it gets converted to a different crystalline form, known as Cellulose II.

During mercerization also, some native cellulose gets converted to cellulose II. The extent of this conversion depends on process conditions like temperature, tension, NaOH concentration etc.

In the table given below, the dimensions of unit cell of cellulose I and II are given:

| **Crystal form** | **Dimension a (Å)** | **Dimension b (Å )** | **Dimension c (Å )** | **B (degrees)** |
|---|---|---|---|---|
| Cellulose I | 8.35 | 10.30 | 7.9 | 84 |
| Cellulose II | 8.14 | 10.3 | 9.14 | 62 |

The figure below arrangement of cellulosic chains in crystalline register in cellulose I and II respectively. It is easy to see that the formation of intra and inter chain hydrogen bond formation in the two crystalline forms.



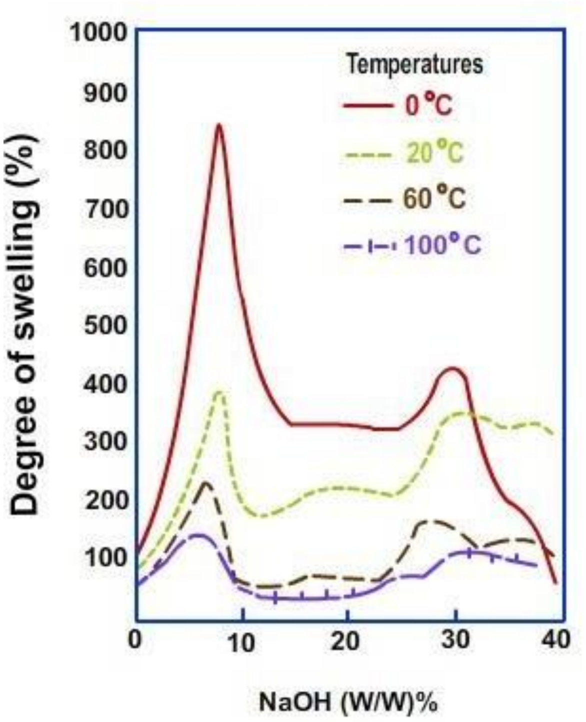
**Swelling of cellulose fibres in Alkali solutions**

It must be clear that mercerization involves disruption of crystalline part of cellulose. For this to happen, alkali solutions of sufficiently high concentrations which can form alkali hydrates of such sizes which can enter the crystalline phase must be employed. Swelling occurs during mercerization but it is not the sufficient condition for mercerization to take place.

This will be clear from the figure shown below which shows swelling of cotton fibres with different alkali concentrations at different temperatures.

Cellulose--model films and the fundamental approach. Eero Kontturi, Tekla Tammelin, Monika Osterberg

Chemical Society Reviews , 35(12):1287-304: 2007;



**Swelling of cotton fibres at different alkali concentration and temperature**

In the figure, the first sharp peak due to swelling appears at around 10% NaOH concentration. This could be very high at low temperatures. In fact, if viscose was to be treated with 10% NaOH solution at 0 °C, it will dissolve!

The swelling occurring at this concentration is solely due to amorphous swelling and does not result in any of the effects associated with mercerization. It is temporary in nature, but can cause large shrinkage due to high degree of swelling involved.

At higher concentrations, the swelling goes down and increases again at around 30% concentration. This swelling is caused by disruption of crystalline phase of cellulose. Generally the mercerization is carried out at 18-24% NaOH concentration and the swelling caused is much less than that occurring at 9-10% NaOH concentration. Hence it can be concluded that swelling is necessary but not the sufficient condition for mercerization to occur.

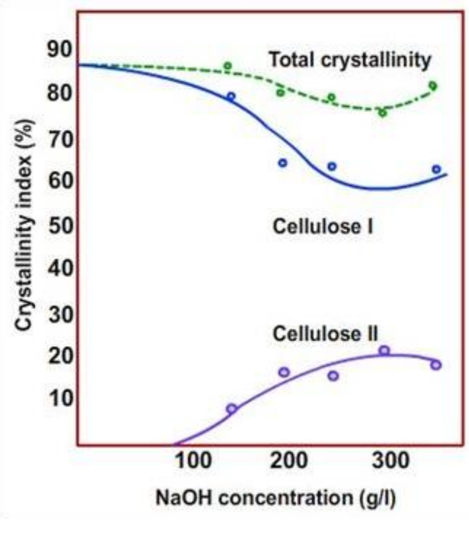
The effect of mercerization on various physical and other properties of cotton is discussed in following sections.

## Structural Modification

### Effect of NaOH Concentration

It has been discussed that mercerization leads to conversion of cellulose I to cellulose II. Native cellulose is Cellulose I and regenerated cellulose (example – viscose) is cellulose II. However, during mercerization, conversion of cellulose I to cellulose II is only partial. Hence mercerized cotton is a combination of both crystalline forms. The extent of conversion is dependent on various process parameters like concentration of NaOH, time of treatment, temperature and tension employed in the process.

In the figure given below, the effect of NaOH concentration on crystallinity of cotton is given (time 60 sec, temp 20 °C, tension- to maintain length change=0%)

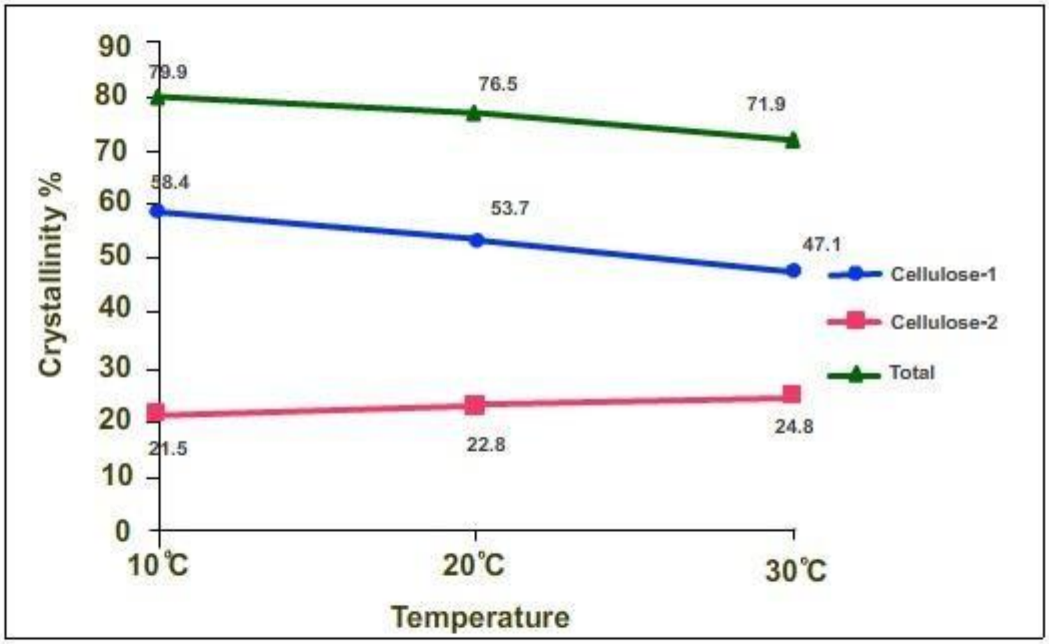


### Effect of alkali concentration of crystallinity of cotton

From the figure it can be inferred that the formation of cellulose II is favoured at higher alkali concentrations. The overall crystallinity of cotton also goes down slightly on mercerization.

### Effect of temperature

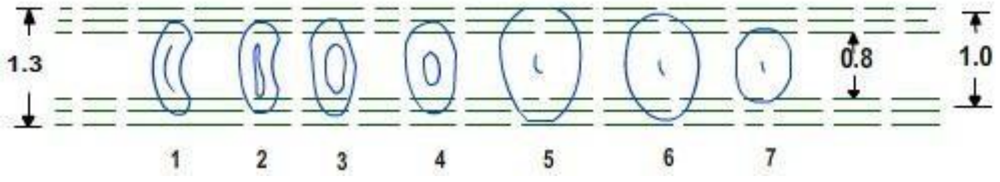
Temperature seems to have a similar effect on conversion of cellulose I to cellulose II. Overall crystallinity also goes down. This is shown in the figure below:



**Effect of temperature on crystallinity of cotton (time 60 sec, temp 20 °C, tension- to maintain length change=0%)**

### Enhancement in lustre

Cotton owes its non lustrous appearance to its non uniform twisted, convoluted, bean shaped fire cross section. As there is continuous change in the fibre cross section along its length, it has poor specular reflection which is responsible for high lustre. On mercerization, the fibre swells gradually and the false twist and the convolutions gradually disappear. The cross section becomes almost circular and the fibre acquires the shape of a regular uniform cylinder. This process of gradual change in the fibre cross section is depicted in figure below:



**Gradual change in cross section of cotton fibre on mercerization**

In the above figure, stage 1-5 show swelling of cross section of fibre. It is easy to see conversion of a bean shaped flat cross section to almost round shape and gradual disappearance of lumen. Stage 6 and 7 are associated with removal of NaOH from fibre on washing and drying. It is important to note that on loss of sodium hydroxide during washing and subsequent drying, the fibre shrinks in cross sectional area, but maintains its rounder shape. Overall, there is very little gain in fibre volume due to mercerization, and hence the density of the fibre remains unaffected.

The rounder, more uniform (convolution-less) and regular cross section results in more specular reflection which results in higher lustre. However, it must be noted that the process of removal of convolutions and other surface irregularities (wrinkles and creases) is greatly aided by tension. Hence tension mercerization always results in more lustrous product as compared to a slack mercerized one.

The presence of protruding fibre ends on the yarn surface suppresses lustre. Hence cotton yarns meant to provide high lustre must also be singed in order to maximize lustre.

**Mechanical properties**

Mercerization has been found to increase the tensile strength of cotton fibres even though a drop in overall crystallinity is recorded. The main reason for this phenomenon to occur is swelling of fibres. The presence of many convolutions and false twists in the fibres cause weak spots to be present. These weak spots act as zones of stress concentrations due to lower cross sectional area on application of a tensile stress. Swelling, which is an integral part of mercerization process, removes convolutions and false twists and the fibres acquire a more uniform cross section along its length. With weak spots gone, the fibres exhibit enhanced tensile strength as compared to a non-mercerized fibre.

**Increase in tensile strength can be summarized as:**

- Removal of convolutions results in removal of weak spots at the point of reversal
- Fibres have more uniform, circular and smoother cross section after mercerization
- The fibrills are arranged parallel along the fibre axis

- Fibre alignment along fibre axis is better in case of tension mercerization as compared to slack mercerization

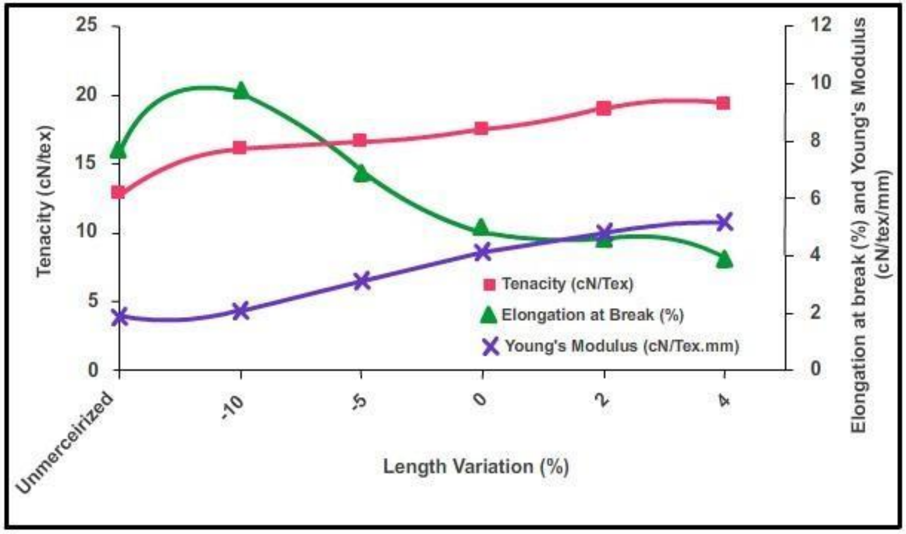
### Effect of tension

Mercerization has a significant effect on mechanical properties of cotton. In the figure given below, tenacity, breaking elongation and Young's modulus of cotton mercerized with 300 gpl NaOH solution at 20 °C for 60 sec are plotted. The tension is varied to allow 10% shrinkage to 4% stretch. The elongation and modulus are indicated on secondary vertical axis. It is clear that the enhancement in both tenacity and modulus is higher at higher tension. It is easy to visualize this since it results in better alignment of molecular chains in fibre axis direction (higher orientation). However, in case of elongation, it is reverse. With increasing tension, the elongation at break decreases monotonically. It is to be expected as increasing orientation would lead to lower elongation. At negative tension though (shrinkage occurring) the breaking elongation is higher than that of unmercerized cotton.

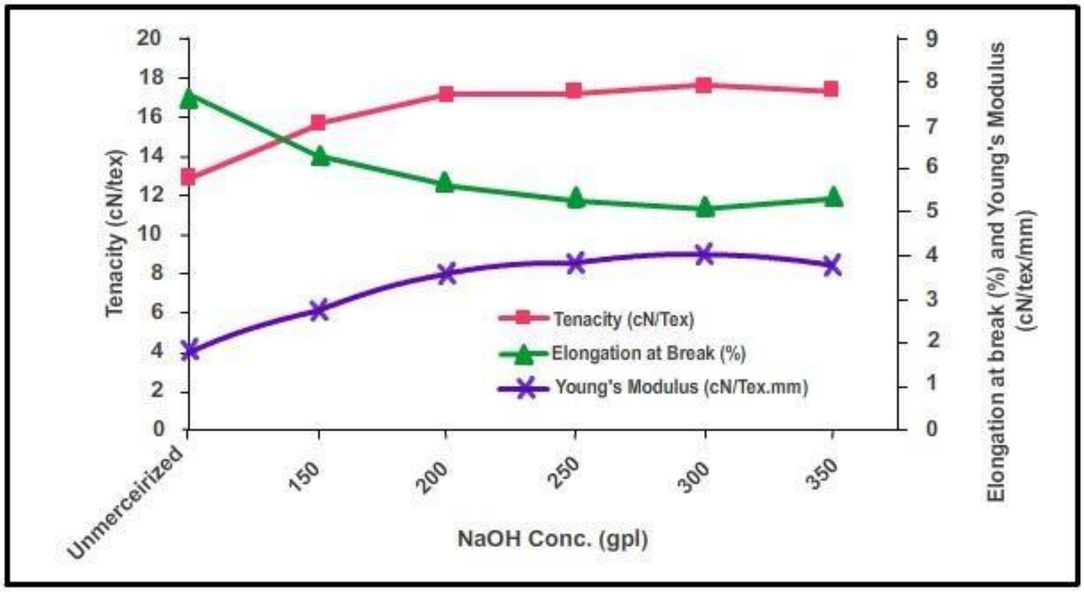
Hence it can be concluded that if improving the tenacity of cotton yarn is the main objective, mercerization should be carried out under tension.

### Effect of Alkali concentration

The effect of alkali concentration on tenacity, breaking elongation and Young's modulus of cotton mercerized with NaOH solution of variable concentration at 20 °C for 60 sec at constant length are plotted in the figure given below. The alkali concentration is varied from 100 to 300 gpl. Again, the elongation and modulus are indicated on secondary vertical axis.



**Effect of Tension on Mechanical Properties of Cotton Yarn during Mercerization**



**Effect of NaOH conc. on Mechanical Properties of Cotton Yarn Mercerized at Constant Length**

**Dyeing Properties**

Since mercerization results in change in physical structure of cotton, as manifest in change in crystal structure, crystallinity and lustre, it affects the dyeing behavior of cotton. The important changes that cause this are:

- Mercerization decreases the crystallinity (increases amorphous content)
- Modifies the texture

Overall effect – greater moisture absorption, greater reactivity towards chemical reagents and dye molecules

Mercerized cotton has higher

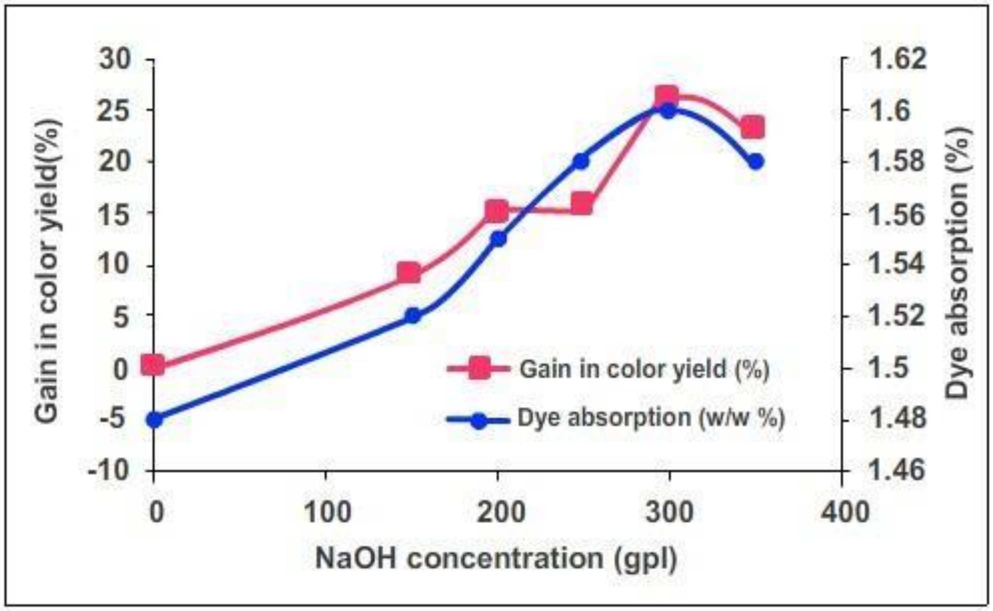
- Dye absorption ( dye pickup)
- Rate of dyeing
- Visual colour yield as compared to unmercerized cotton

Improvement is more marked in slack mercerization (lower tension)

Increase in colour yield can allow for a saving of 15-50% in dyestuffs. Indeed many times, this is the reason for subjecting cotton goods to mercerization.

**Interesting -** mercerized cotton appears darker than unmercerized cotton even when the dye absorption is same.

The effect of mercerization on dye absorption and apparent color yield is shown in the figure below. The concentration of sodium hydroxide is varied from 150 to 350 gpl.



**Effect of Mercerization on Dyeing Properties of Cotton Yarn at constant length (dye- CI Direct blue 1)**

The increased Visual color yield (darker shade) of mercerized cotton is due to increased dye absorption as well as the optical effect.

**Kubelka Munk Equation**

Defines the colour yield in terms of reflectance of dyed material

$$\frac{K}{S} = \frac{(1 - R)^2)}{2R} = \frac{aC}{S}$$

***K*** – Light absorption factor, ***S*** – light scattering factor, ***C*** is concentration and ***a*** is a constant

***R*** - reflectance

***K*** changes linearly with concentration (within some limits)

Upon mercerization

1. ***S*** decreases (less internal scattering from a rounder x-section)
2. Non uniformity of the operation causes increase in colour yield (apparent)

Non-uniformity of the mercerization results in peripheral fibres absorbing most of the dye. This may cause the cotton goods to appear darker in shade.

If improving the dyeability is the only aim then 150-190 gpl NaOH treatment is ideal.

In general, the increased dye absorption and the optical effect may contribute roughly equally towards increased Visual colour yield after mercerization.

**Wetting agents for mercerization:**

Mercerisation liquor of concentrated NaOH solutions is generally applied at low temperatures (15-20 °C). Under these conditions, liquors possess high viscosity and swelling of fibers is high and rapid. This results in poor and non uniform penetration of cotton textiles by NaOH solutions.

Sometimes goods are mercerized in greige or non-scoured state. The presence of sizes or cotton waxes further hinders penetration of NaOH in the cotton yarns/fabric. Therefore the use of wetting agents to increase the wetting of goods by mercerizing liquor is resorted to, which results in faster and more uniform treatment of cotton goods.

since the liquor is highly alkaline, the prospective wetting agent must be:

- Soluble and stable in alkali solutions of mercerizing strength
- Should be efficient (effective at low concentration)
- Should have low affinity to fiber
- Should be low foaming

Normal wetting agents are not sufficiently soluble in moderately concentrated caustic soda solution. Products based on cresylic acid (a mixture of o-, m- and p-cresols) were used sometime back. However these are toxic and non-biodegradable in nature and its use in mercerization in on wane. Addition of solvent additives such as alcohols (e.g. cyclohexanol), ethers, ketones, lower fatty acid amides increases wetting power of mercerizing liquor.

**The biodegradable wetting agents**

- Certain alkylarylsulphonates
- some organophosphonates (e.g. sodium methyloctylphosphonate)
- alkylated diphenyloxide sulphates (e.g. dodecyldiphenyloxide sulphate)
- especially sulphated aliphatic alcohols (e.g. 2-ethylhexyl sulphate). *most effective have chains with 4-8 carbons*
- Example: sulphated 2-ethylhexanol, activated with about 10% butanol and unsulphated 2-ethylhexanol.

**Hot mercerization**

Although mercerization is an exothermic process and is more efficient at lower temperatures (typically a temperature range of 15 to 20 °C is used), it has following drawbacks:

- At lower temperatures, NaOH solution of mercerizing strength has high viscosity and surface tension
- When a yarn/fabric is mercerized, swelling of fibres at yarn surface due to mercerization causes compaction of yarn structure
- This results in poor penetration of NaOH solution in the core of yarn
- The treatment becomes non-uniform

The basic problem of poor penetration leading to non uniform mercerization can be tackled by carrying out mercerization with hot (60 to 100 °C) NaOH solution of mercerizing strength. This is known as hot mercerization.

However, since mercerization won’t take place at high temperature, the temperature of the treated fabric has to be brought down.

Therefore, hot mercerization becomes a two stage process, in which the first stage is treatment of cotton fabric with hot NaOH solution of mercerization strength and the second stage is the reduction in temperature of the treated fabric to bring about the mercerization.

As the temperature of the fabric is brought down, swelling may start and the fabric may shrink and hence the dimensions may need to be maintained during cooling stage by desired applied tension.

**Advantages:**

- Hot NaOH solution has low viscosity and higher penetration power
- Swelling of cotton fibres in hot NaOH solution is low, hence more uniform treatment

- Faster process, leading to: higher productivity and compact unit
- Period of contact between material and NaOH can be reduced by upto 50%
- The fabric can be stretched to greater degree as the fabric becomes more plastic
- More uniform coloration
- Better dye uptake (less colour yield)
- Can permit elimination of scouring process

However, under conditions prevailing in hot mercerization, degradation of cellulose at high temperatures in presence of air can take place.

**The sequence**

- Saturation of cotton with NaOH under relaxed conditions (50 oC to boiling point) for 4-20 seconds
- Controlled hot stretching
- Cooling the stretched material to less than 25 °C temperature
- Tension controlled washing (till NaOH concentration in fabric falls below 60 gpl level)
- Final washing under relaxed conditions

Since NaOH is also an agent for carrying out scouring of cotton fibre, yarn/fabrics at high temperatures, hot mercerization can also be suitably modified to carry out both mercerization and scouring in one operation.

**Sequence for combined mercerization and scouring**

- Hot saturation of fabric with alkali solution
- Steaming of relaxed or stretched material for
- 10 min at atmospheric pressure
- 5 sec under pressure (130-140 °C)
- Cooling and mercerization
- Washing

There is another variation of hot mercerization. The sequence is as follows:

- Washing of fabric at 95 °C
- Hot squeezing (high speed steam injection)
- Impregnation in NaOH at 20 °C
- Impregnation in NaOH at 30 °C
- Stabilization under tension
- Washing

The advantages of this variant are:

- More uniform treatment faster process, hence process time can be reduced
- More productivity or more compact unit
- Higher stretching is possible; this will result in higher mechanical strength/lustre
- Higher stretch is possible if stretching proceeds while cooling
- Uniform dyeability

***Dyeuptake is better but colour yield is lower***

**Mercerization of blends**

Sometimes blends of cotton and viscose need to be mercerized to bring dyeuptake and lustre of cotton at par with that of viscose

**Problems faced in mercerization of cotton/viscose blends**

Solubility of viscose in alkaline solutions causes weight and strength loss

Dissolution occurs at 80-130 gpl concentration of NaOH

(Viscose becomes highly swollen)

This problem can be solved by using a modifying sequence of mercerization as described below:

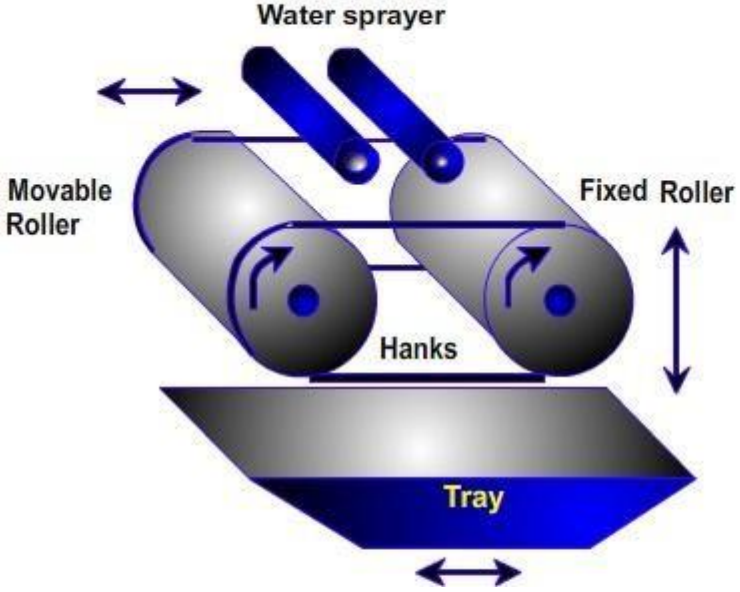
- Hot impregnation (saturation with hot mercerization liquor to minimize swelling of viscose)
- Addition of electrolyte in the mercerizing liquor
- Use of KOH or admixture of NaOH and KOH (KOH induces less swelling)
- HOT water rinse (at 90 °C); viscose solubility is less at higher temperature
- Addition of electrolyte (NaCl) in rinsing bath (electrolyte suppresses swelling of viscose)

**Machines for Mercerization:**

**Fabric Mercerization with Tension**

1. Stenter type or chain mercerizing machine
2. Chainless mercerizing machine

3. Chainless and pad less mercerizing machine



**Hank Mercerizing Machine**

### Yarn mercerization

Yarns are mostly mercerized in hank form. Yarn mercerizing machines generally consist of two rollers, on which the hank can be mounted. A device can be used to apply tension (to stretch) on the hanks. After the hanks are mounted, the rollers can be lowered into a tray which consists of caustic soda solutions of mercerizing strength. The hanks are allowed to saturate with alkali, the tension is generally applied later. After sufficient time is allowed for mercerization (1-2 min) the hanks are squeezed and rinsed. The tension is released once the residual alkali concentration drops below 60 gpl. For optimum gain in tensile strength and lusture, a tension causing stretch of 0.5-3% is applied, higher tension results in lower tensile strength.

### Fabric mercerizing machines:

Fabric mercerizing machines are generally continuous operation machines with the ability to apply controlled lengthwise tension. There are mainly two types of machines:

1. Those equipped with a chain to apply a controlled width wise tension (**Pad chain mercerizing machine)**

2. Chainless machines, which apply the width wise tension by means of expander bars or bowed roller (**Chainless mercerizing machine)**

**Pad chain mercerizing machine**

In these machines fabric is saturated with alkali solution and padded. The saturated fabric passes over a set of rollers (airing rollers) which allows the swelling or mercerisation to take place. Fabric is again saturated and squeezed and passed into a stenter where length and width wise tension is applied. Width wise tension is applied using stenter clips on chain.

This is followed by sprinkling of fabric with water to remove alkali. The tension is maintained till the alkali concentration drops below 60 gpl. After this, fabric can be rinsed and neutralized in open width washing machine (Tension may be relaxed).

The tension applied by means of clips in weft direction can be higher which can impart higher lusture to the fabric. However the tension in width wise direction can cause the fabric to expand in a non uniform way, as shown in the figure below. Also there is a risk of fabric getting torn near the edges where it is held by clips.

Chainless mercerizing machine tackle above problem by using bowed rollers (figure below) to apply width wise tension. The clips of chain mercerization machine are replaced by an expander unit consisting of bowed rollers. The stretch or tension applied in weft direction is determined by warp wise tension in the fabric which in turn is controlled by oscillating rollers. Other features are more or less similar to chain mercerization units.

**Determination of degree of mercerization:**

Although there are many methods to do this, one quantitative test based on the ability of mercerized cotton to absorb barium hydroxide is widely used. Mercerized cotton can absorb more Barium hydroxide than un-mercerized cotton and this is the basis for this test. The test method is described below:

Mercerized and un-mercerized cotton samples (2 gm each) are treated with 30 ml of N/4 Barium hydroxide for two hours in conical flasks at room temperature. Preferential absorption of barium hydroxide by cotton samples reduces the strength of Barium Hydroxide solutions. The amount of $Ba(OH)_2$ absorbed can be determined by taking 10 ml of $Ba(OH)_2$ solution from each of the flasks and titrating it with N/10 HCl, phenolphthalein being used as an indicator. Fresh $Ba(OH)_2$ is also titrated (blank titration) to accurately assess the actual $Ba(OH)_2$ in solution.

The Barium Activity Number is given as:

BAN = (B-M) / (B-C)*100

Where B = Volume of HCl (ml) required for blank titration

M = Volume of HCl (ml) required with mercerized cotton

C= Volume of HCl (ml) required with un-mercerized cotton

For completely mercerized cotton the value of BAN is around 155 and for semi mercerized cotton it varies in between 115 and 130.

# MODULE – V

# WASHING & DRYING

## 5.1 IMPORTANCE OF WASHING

### Washing in Textile

Rinsing and washing are the operations carried out most frequently during a complete textile finishing cycle. They are almost always connected to key treatments and aimed at removing from the fabric insoluble matters, matters already in solution or an emulsion of other impurities. During the fabric preparation process, for example, washing is carried out after desizing, boiling and other bleaching and mercerising processes; in dyeing, the washing stage is necessary to complete the dyeing process itself or to eliminate the dyestuff which has not been fixed; during the printing stage, washing performs a finishing action. When using vat dyes or disperse dyes, the washing process aims at removing insoluble pigment substances from the fibre surface by means of wetting or dissolving agents.

This could therefore be considered a crucial treatment in the whole textile process, because of the frequent use and strong economic impact. Manufacturers increasingly focus their attention on reducing water consumption, which leads to subsequent energy and hot water saving as well as a reduction in wastewater. Together with traditional washing systems with vats equipped with "vertical cylinders" the market offers horizontal washing units, which reduce the liquor ratio and the energy and water consumption for each kilogram of washed material.

Washing includes a chemical-physical process, which removes the dirt from the substrate, and a series of physical operations aiming at improving the "feedback action".

**The sequence of the various washing steps is the following:**

a. Formation of the detergent liquor (transfer of matter + energy by mixing);
b. Reaching of the process temperature and wetting (transfer of the liquor to the material);
c. Separation of impurities and emulsification (transfer of matter from one step to the other);
d. Removal of the liquor from the fibre (transfer of macroscopic matter);
e. Drying (interstage transfer of heat and matter).

Often these steps occur simultaneously. The use of surfactants (detergents) during the washing stage is extremely important to speed up the wetting of the textile material, to facilitate the removal of dirt from the substrate, thus keeping the emulsion inside the liquor and preventing the particles laying down again on the fibre.

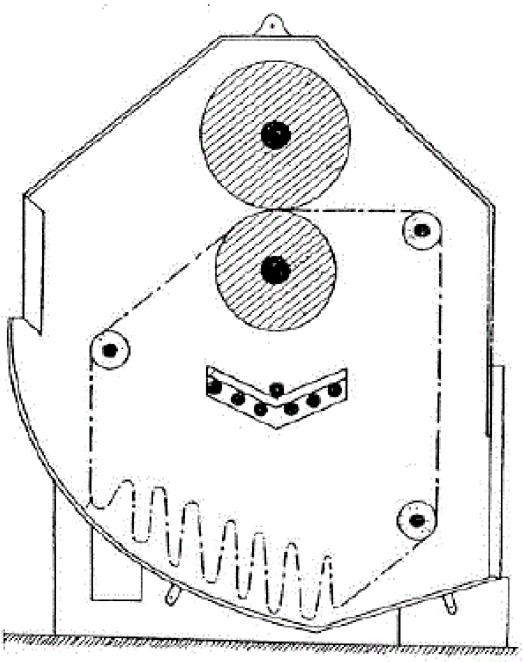
Crucial factors are water (which must be quite soft to avoid precipitation of Ca and Mg salts which could give a rough and coarse hand to the textile) and chemical products to be used (emulsifying agents, softening agents and surfactants).

## Types of Washing:

Washing can be performed on fabrics either in open-width or in rope form. Rope washing is more effective than open-width washing thanks to a stronger mechanic action, which favors the cleansing, and the relaxation of the fabric structure; for delicate fabrics an open-width washing must be preferred to avoid marks and creases. Open-width washing is also the best choice for processing huge lots.

### Rope Washing

Substantially, batch piece washing machines are made up of a couple of squeezing cylinders, which make the fabric swell (the fabric is previously sewn on top and bottom and takes the shape of a continuous ring); these cylinders are assembled inside a vessel, whose lower part contains the detergent liquor. It is possible to wash a fabric inside this vessel, by feeding it into restricted area without laying it stretched out.



**Rope washing machine**

The efficiency of this operation is enhanced by the mechanic action, which facilitates both detergency and tension relaxation. This operation is highly cost-efficient because open-width washing allows only one working position and therefore only limited loads can be processed (max. 180 kg) while a rope washing machine can include from one to eight ropes, with an overall weight exceeding 600 kg. Furthermore rope washing machines grant reduced operating times thanks to a more effective mechanic action.

## Open-width Washing

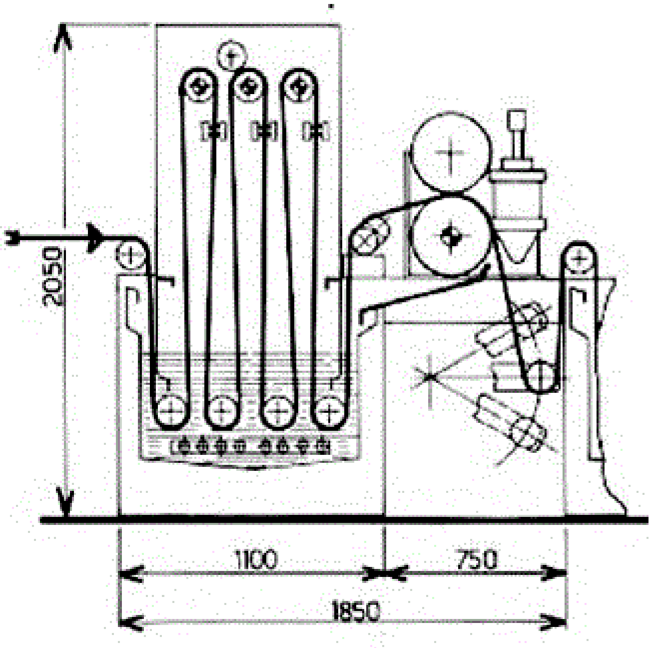
An open-width washing machine is usually a system featuring a vertical path washing with driven cycle of multiple action baths, with a resulting 30/40% water and steam saving. This operating unit is manufactured in several versions (10-15-30 meters) and can be used for every kind of preparation and finishing treatment. Four different washing actions alternate inside this machine:

1) Washing on rising paths;

2) Washing on sloping-down paths, carried out by means of spray nozzles, which atomise on both face and back of fabrics, performing a strong penetration action;

3) "Vibraplus" effect washing, which removes from the fabric the threadlike elements (fibrils) that do not dissolve in water;

4) Extraction washing by means of vessel intermediate squeezing. The longitudinal tension of the fabric remains perfectly unchanged on the whole path; it can be adjusted between 5 and 20 kg by means of upper cylinders equipped with self-adjusting control system which generates a sliding motion crease-and-fold proof also on extremely delicate fabrics. Plush fibrils are removed from the vessel with no need for brushes or liquor dilutions.



**Open-width washing machine**

Another type of machine divides the washing process into single steps, which are systematically repeated. In this way the whole process can be not only constantly monitored but also accurately calculated.

## 5.2 OBJECTS OF DRYING

### Drying:

In wet processing industry drying is used after de-watering of fabric. In textile finishing unit; dryer uses for dry the knit, woven fabrics and dyed yarn. We can define drying as a process where the liquid portion of the solution is evaporated from the fabric.

### Objects of Drying:

1. To dry the fabric with help of steam
2. To control the shrinkage
3. To prepare for next subsequent process
4. To dry tubular and open width fabric without tension

### Drying process in textile industry:

Drying is very essential in textile industry to eliminate or reduce the water from the fibers, yarns and fabrics following wet processes. Drying happens when liquid is vaporized from a product by the application of heat. Drying, in particular by water evaporation, is a high-energy-consuming step although overall consumption may be reduced if re-use/recycling options are adopted.

### Drying methods:

Fiber, yarn or fabric can be dried with mechanical or thermal process. Mechanical processes are used in general to remove the water which is mechanically bound to the fiber. This is aimed at improving the efficiency of the following step. Thermal processes consist in heating the water and converting it into steam. Heat can be transferred by means of:

1. Convection
2. Infrared radiation
3. Direct contact
4. Radio-frequency

Drying techniques depend on packages. Loose fiber can be dried in three ways:

- Centrifugal extraction
- Mangling
- Evaporative drying

In other way, hanks may be dried by employing a dehumidifying chamber. Moisture is recovered by condensation, using conventional de-humidification equipment. In comparison to evaporative dryers, yarn residence time tends to be longer, but energy consumption is lower.

### Yarn packages drying:

The moisture of dyed packages is initially reduced by centrifugal extraction. Specially designed centrifuges, compatible with the design of the dyeing vessel and yarn carriers are employed.

### Fabric drying:

The drying process for fabric usually involves two steps: the first one is aimed at removing water which is mechanically bound to fibres, while the second one is necessary to dry completely the fabric.

1. Hydro-extraction by squeezing
2. Hydro-extraction by suction
3. Centrifugal hydro-extractor
4. Stenter process

## 5.31 WORKING PRINCIPLE OF HYDROEXTRACTOR

### Hydro Extractor and Hydroextraction Process:

Hydro-extractors are machines which are used in textile processing industry. It is also known as centrifugal machine. Hydro extractor machine is used for removing excess water from fabric by centrifugal extraction. About 65% water is removed by this process. It plays an important role after passing dyeing section.

**Fig: Hydro extractor machine**

Hydroextraction process removes the water (the water quantity varies according to the type of fiber) dispersed in the fibers by mechanical action; this process aims at reducing energy consumption and is carried out before the final fabric drying or between the various wet processing stages (washing, dyeing).

**Working Principle of Hydro Extractor Machine:**

Hydro extractor can be carried out in the following ways:

**1. Squeezing:** The water dispersed on the surface and in the spaces of the fabric is removed by means of the pressure applied by two cylinders.

**2. Centrifugation:** This process eliminates the greatest quantity of water dispersed on the surface of the textile by centrifugal force. It is applied above all to resistant yarns, knitted goods and fabrics.

**3. Steam pressure:** A high-speed steam jet blown on the whole width of the stretched fabric passes through the cloth and eliminates the water in excess. Extracted water and steam are condensed and reused.

**4. Vacuum:** This method applies vacuum technology and is used to dry very wet fabrics or delicate fabrics that do not stand up to the pressure of the cylinders of a squeezing unit, which could negatively affect the surface structure. The stretched fabric slides open-width above the opening of a cylinder-shaped structure connected to a suction system. The air drawn from outside removes the exceeding water when passing through the textile cloth.

**Advantages of Hydro Extractor:**

- No deformation of the packages.
- Excellent rewinding properties. Rewinding can even be eliminated in a lot of cases.
- Low residual moisture.
- Even humidity distribution through the package.
- Low energy consumption.
- Dyeing tubes last longer.
- Processes many different size packages.
- Operator of centrifuge can also load dryer.
- Maintenance-free brakes.
- Closed system for effluent.
- Low compressed air consumption.
- Significant energy savings.

## 5.32 MULTI CYLINDER DRYING

1. In this type of m/c, the drying unit consists of 5 to 7 or 11 cylinders having same diameter are used.
2. All cylinders may be steel cylinders or first two cylinders are teflon coated & rest of are steel cylinder.
3. The cylinders are heated by passing steam.
4. Heat in initial cylinder is low & gradually increases when moved towards final cylinder.
5. If large amount of heat is given to the initial, the sized may be backed.
6. If finer yarn is used, then no need to use excess cylinder.

**Multi Cylinder Drying**

**Advantages:**

1. High speed process.
2. Uniform drying.
3. Non- sticky so smooth drying.
4. Drying efficiency high.
5. Less time required.

**Disadvantages:**

1. For high viscosity, stick properly may observed.
2. For friction, yarn hairiness.
3. Shinning effect.
4. Yarn shape may hamper.
5. Possibility of yarn flaten.

## 5.33 INFRARED DRYING:

- In this machine, the heating chamber consists of a plate which is constantly heated by gas flame.
- The warp sheet is passed over the plate & dried in the process.

- When gas flames are not used, then electronic plate may be used.
- Arrangement should be made to throughout the moisture removed from the yarn. This m/c is not used signally.
-

**Advantages:**

1. No shining effect.
2. Drying efficiency high.

**Disadvantages:**

1. Yarn may burn.
2. Higher cost.
3. Difficult to maintain uniform heating.
4. Risk of accident

## 5.34 RADIO FREQUENCY DRYING

Conventional mode of Drying Textiles after they have been dyed is a slow process. Textile industries can increase throughput and fill orders more prominently using Radio Frequency (RF) Dryers. RF system has capability to accelerate the drying process and shorten production time. RF drying offers high volume, high speed and high quality drying which is what is exactly needed in textile industries. As wet garments of acrylic, cotton, nylon and polyester blends pass through the drying chamber, the radio waves vibrate the contained water molecules million times per second, vaporizing them. Ventilator fans are used to remove damp air from the drying chamber.

The dryer system comprises the 125kW industrial high frequency generator in conjunction with a drying chamber incorporating an electrode applicator and air extraction system. The equipment is suitable for drying most types of fibres which have had prior mechanical moisture extraction in either, cone, muff, bump or loose stock form. Many types of fibre can be dried. The machine incorporates a modular polypropylene conveyor band and conveyor system.

Because the RF waves concentrate in the wettest, densest portion of the garments, RF drying has a leveling effect that practically eliminates any problems of uneven shrinkage and over drying. The RF drying times depend on the type of fabric; the percentage of moisture in the fabric going in to the dryer, and the degree of dryness desired.

**Advantages:**

The major advantage is that it gives thorough, consistent drying in less lime and also occupies less space. In addition to these, following advantages are prominent:

1. Faster Drying
2. Faster Productionn.
3. Energy Saving
4. Less Down Time
5. Lower Maintenance
6. Less work in progress
7. Space savings