LECTURE NOTE

SUB: TEXTILE CHEMICAL PROCESSING - I

BRANCH: - TEXTILE ENGG.

SEMESTER: 3ʳᵈ

GOVERNMENT POLYTECHNIC, BHADRAK

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<u>SYLLABUS</u>

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    1.3 Singeing, Different methods of singeing (Plate, Roller and Gas Singeing), drawbacks and   advantages.

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    2.1 Object, types, method details and mechanism of removal of starch.
    2.2 Efficiency of desizing,

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    3.2 Scouring of textile & evaluation of scouring efficiency.
    3.3 Scouring of natural, man-made and blended textiles.
    3.4 Degumming of silk.
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  Wool by acid dye).
    5.6 Working principles of Winch, Jet, Beam, Hank and Package dyeing machine, Jigger, J-Box

UNIT- I
DRY PROCESSING

1.1 PRE-CLEANING, MENDING, STAMPING, STITCHING, SHEARING AND CROPPING.

INTRODUCTION
After the grey fabrics have been received in the grey room by the finishing enterprises, the bales are opened and inspected, a process which is increasingly mechanical, but much of it remains subjective. The most important point is to obtain fabrics" free from exterior impurities" in order to achieve smooth and trouble-free results in the subsequent finishing systems.

INSPECTION
It is checked whether the grey fabrics are in conformity with standards, and all weaving faults are marked out. Fabric inspection involves three possible steps:
1. Perching,
2. Burling
3. Mending.

1. Perching,
Perching is a visual inspection and the name derives from the frame, called a perch, of frosted glass with lights behind and above it. The fabric passes through the perch and is inspected. Flaws, stains or spots, yam knots and other imperfections are marked.

2. Burling
Burling is the removal of yam knots or other imperfections from the fabric. The faults are then mended and any knots in the material are then pushed to the back.

3. Mending.
Mending is obviously, the actual repair of imperfections. Knotting should be done carefully and thoroughly so that the repair or holes is not visible.

STAMPING
After the goods have been inspected, checked and classed in the grey room, according to quality and stamped.

STITCHING
Goods are sewn together, end to end, by sewing machines especially constructed for this purpose.

PRE-CLEANING OF FABRICS

The pre-cleaning of grey fabrics may be carried out in a separate unit just before cropping and shearing operations. The efficiency of pre-cleaning is the foundation of good cropping and shearing. The pre-cleaning operation is achieved with:

(i) Thorough grinding of the cloth surface by emery covered rollers.

(ii) Scraping with suitable designed and located scraping blades.

(iii) Efficient brushing on both sides of the cloth.

With the progress of grinding and scraping action, the cloth surface gets covered with thread ends, dust, fluff, dirt etc., thus the pre-cleaning unit should have a good dust exhausting system.

BRUSHING

The purpose of brushing is to remove the short and loose fibres from the surface of the cloth. It also removes husk particles clinging to the cloth. Brushing is mainly done to fabrics of staple fibre content, as filament yams usually do not have loose fibre ends. Cylinders covered with fine bristles rotate over the fabric, pick up loose fibres, and pull them away by either gravity or vacuum. The raised fibre ends are cut off during shearing operation. Brushing before cropping minimizes pilling.

SHEARING AND CROPPING

Shearing is an operation consists of cutting the loose strands of fibres from either surface of a fabric with a sharp-edged razor or scissors. By manipulating the shearing, it is also possible to cut designs into pile fabrics. Good cropping is perhaps, the simplest way of reducing the tendency of blended fabrics to 'pill'. In the case of cotton fabrics, in particular, care should be taken to see that the shearing Preparation Before Chemical Processes blades do not scratch the surface of the fabric, which otherwise can cause dyeing defects during subsequent dyeing.

1.2 SINGEING, DIFFERENT METHODS OF SINGEING (PLATE, ROLLER AND GAS SINGEING), DRAWBACKS AND ADVANTAGES.
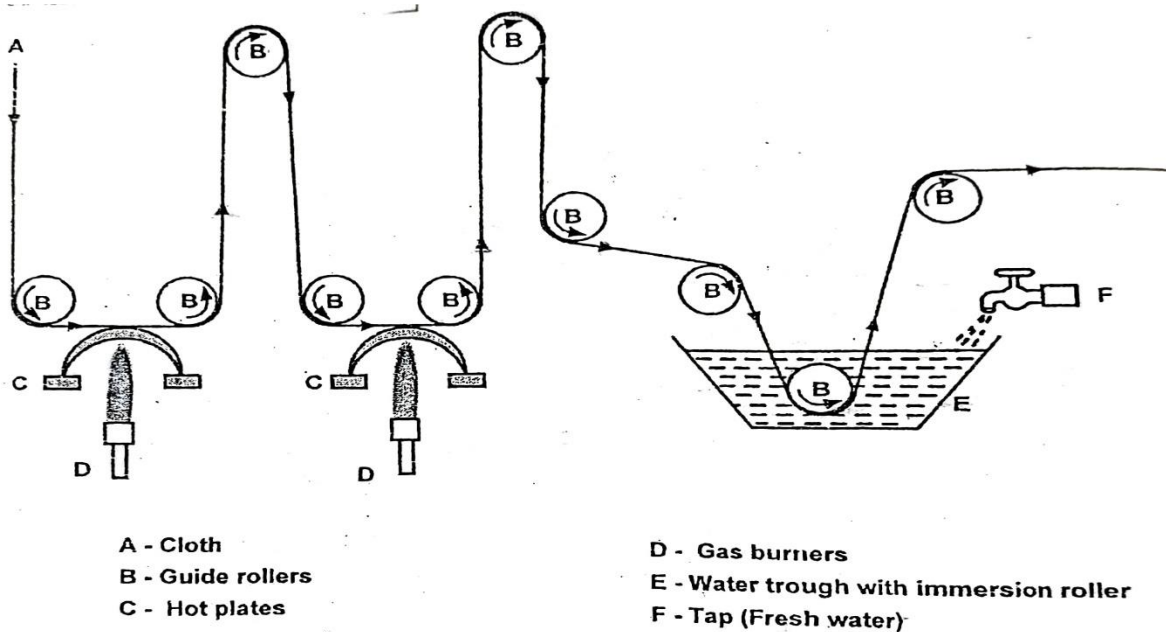
Object of Singeing

Singeing is the process of burning off of protruding fibres from the surface of yarn or fabric in order to improve the lustre and smoothness of the material. The fuzz as the protruding fibres are also called, tends to scatter light incident on the yarn or fabric surface and contributes to a dull appearance of the textile material. Removal of fuzz results in a smoother and more uniform surface that reflects more light and therefore a brighter appearance. Singeing is also referred to as 'gassing', especially when yarn is subjected to this process.

Singeing Machines

Three different types of machine can achieve singeing. These are listed below:

 I. Hot plate singeing machine

2. Roller singeing machine

3. Gas-singeing machine.

1. Hot Plate Singeing Machine

A - Cloth
B - Guide rollers
C - Hot plates

D - Gas burners
E - Water trough with immersion roller
F - Tap (Fresh water)

This machine consists essentially of two or three curved copper plates that are kept red hot by means of heating arrangements under them. As shown in Figure, the cloth to be singed, A, is passed, with the aid of guide rollers B, over the hot plates C (heated by gas burners D) such that the fabric and hot plates are in continuous contact with each other. An automatic traverse motion is fitted to the machine so that the plates change their surface of contact with the cloth as it moves continuously. This helps to prevent cooling of the hot plates due to the same part coming in contact with the incoming cloth at ambient temperature. After passing the last hot plate, the cloth is immediately passed through a water-filled trough E, into which cold water is Continuously flowing from inlet tap F. This 'quenching' is to counteract any tendency of the hot cloth to catch fire.
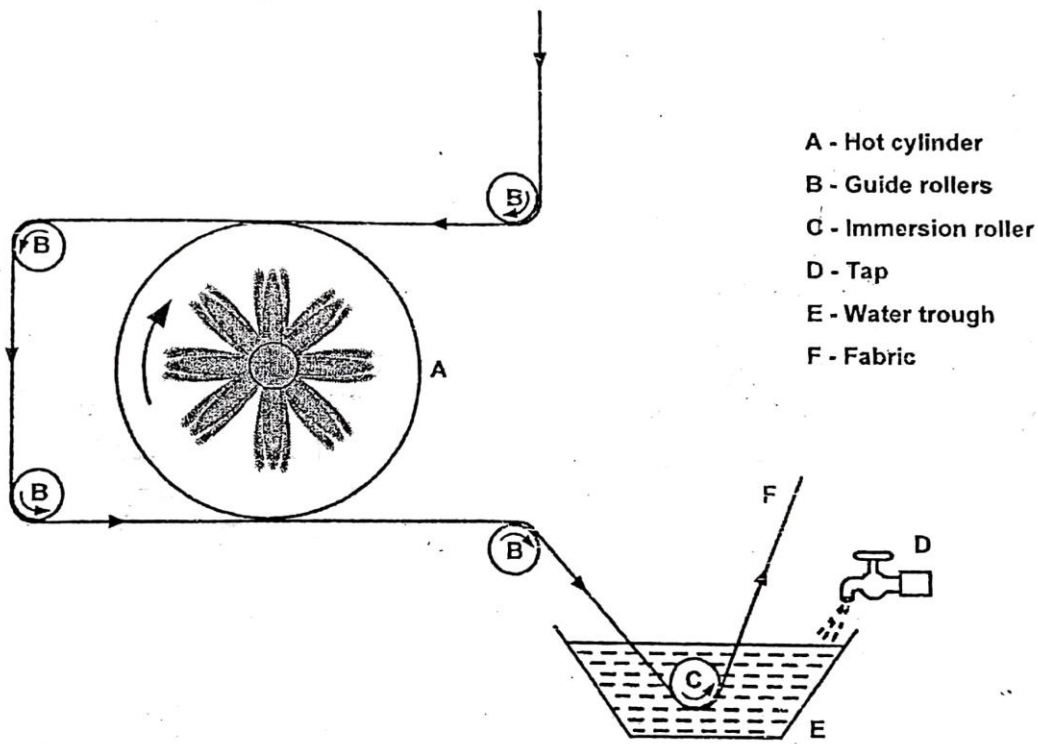
Advantages

Hot plate singeing is suitable for back filling finishing process as the fibre ends in the interstices are not removed.

Disadvantages

1. Fibre ends in the interstices of warp and weft are not signed.

2. Produces an undesirable fabric lustre due to the frictional contact with the hot plate

3. Causes uneven singeing due to difficulty in maintaining uniform plate temperature.
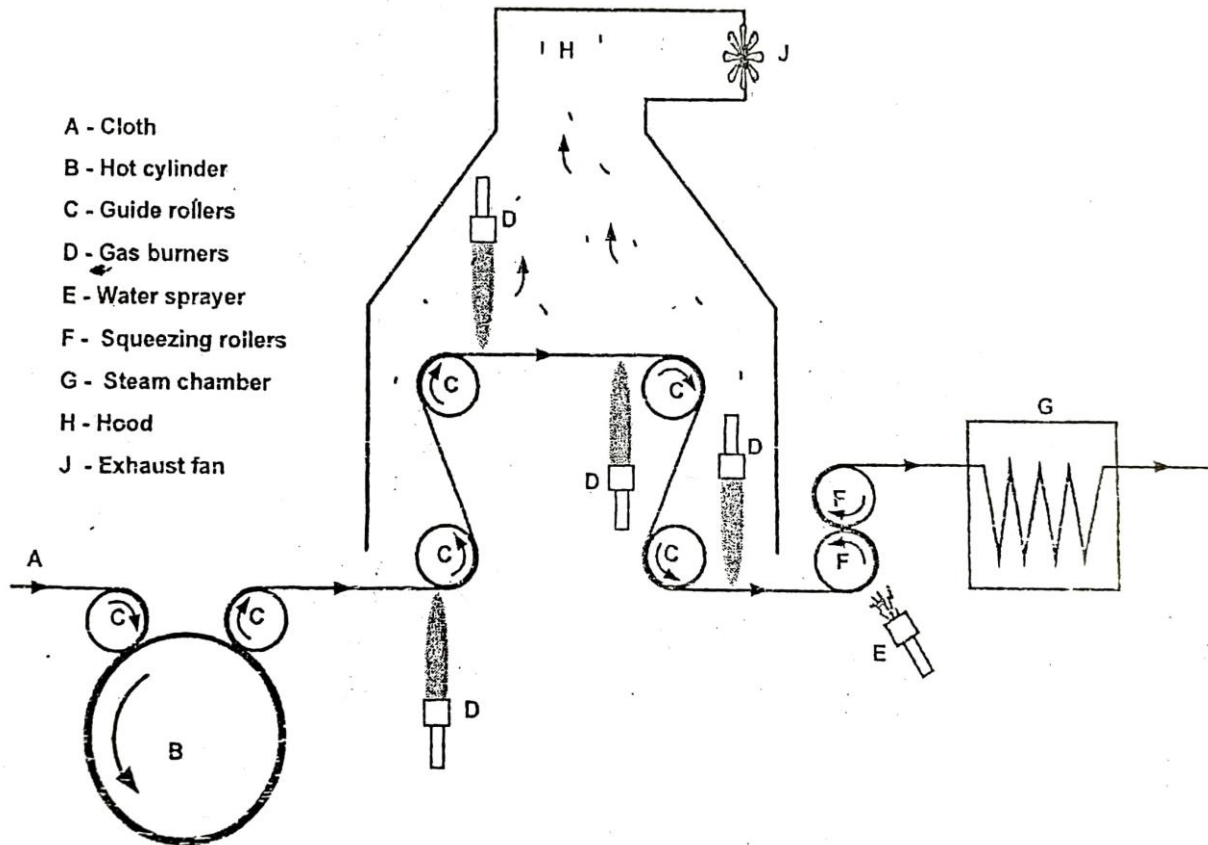
2. Roller Singeing Machine

Roller singeing is similar to hot plate singeing. Here, instead of a hot plate a large cylinder or roller is used. The inside of the cylinder is heated to maintain its outer surface very hot. As shown in Figure, the cloth to be singed F passes around a guide roller B and then over the heated cylinder A, touching its top. It then goes around two more guide rollers to pass under the cylinder, touching its bottom. The guide rollers also serve to keep the fabric under adequate tension. In roller singeing too the cloth is immediately passed into a trough of cold-water E to prevent the hot fabric from catching fire.

A - Hot cylinder
B - Guide rollers
C - Immersion roller
D - Tap
E - Water trough
F - Fabric

The advantages and disadvantages are same as the hot plate singeing machine except that uneven singeing takes place to a lesser extent in roller singeing.

3. Gas-singeing Machine

A gas-singeing machine consists essentially of one or more burners that are designed to produce a continuous, uniform flame by burning a mixture of compressed air and coal or natural gas. The flame issues from a narrow slit that is adjustable with respect to its width and thickness. When the cloth is drawn over the flame at high speed, the flame impinges on its surface and burns the protruding fibres without damaging the cloth. The speed of transmission of the cloth through the singeing machine has to be adjusted to suit the amount of singeing required, without the risk of burning the cloth. The flame is adjusted to be long enough to ensure that when it impinges on the cloth surface the fibre ends present in the interstices of the warp and weft threads are also singed. After passing over the flame, i.e. when the singeing operation is over, the cloth is passed into a trough of water and then through the nip of a two-roll water mangle. This is merely to quench the fabric immediately and extinguish any sparks of fire or glowing fibre ends. Alternatively, the surface of the cloth is hit by a sharp spray of water. In order to remove the burnt fibres and exhaust gases, a hood and exhaust fan are provided over the singeing machine. A typical arrangement using a four-burner gas-singeing machine is shown in Figure. It can be seen clearly that the use of pairs of two slits of gas flame, positioned appropriately, brings about the singeing of both sides of the cloth in just one passage through the machine.

A - Cloth
B - Hot cylinder
C - Guide rollers
D - Gas burners
E - Water sprayer
F - Squeezing rollers
G - Steam chamber
H - Hood
J - Exhaust fan

Advantages

Gas-singeing has the following advantages:

a) Both sides of the cloth are singed simultaneously.

b) Uniform singeing of the cloth is obtained.

c) There is no question of unwanted cloth sheen (lustre) as there is no contact with any metal surface as in the case of the other singeing machines such as the roller and plate types of singeing machine.

d) Fibres in the interstices between the warp and weft threads are also burnt effectively. This is not entirely possible in the case of the other singeing machines.

e) Machine speed van be high and in the range 80 - 125 m/min, a feature not achievable in the other types of singeing machine.

f) The flame can be controlled so as to be equal to the width of the cloth being singed.

g) Different varieties of cloth can be conveniently singed.

Disadvantages

The major disadvantage of gas-singeing is obviously that there is a great risk of fire, if proper care is not taken on this count. However, any risk of fire can be avoided completely, if

a) The flame is adjusted to be at its optimum Size.

b) Careful monitoring of the singeing process is carried out.

c) The necessary fire-fighting equipment is available close at hand, and The operators at the machine are properly trained to run the singeing machine and to use the fire-fighting equipment in an emergency.

Gas-singeing machines- the precautions

The following precautions are vital to safe and proper running of gas-singeing machines

1) Arrangements must be provided such that the supply of gas to the burner is automatically turned off in case the mixture of gas and air does not burn or if, for any reason, the fabric fails to move.

2) An overhead hood should enclose the machine at the top and an exhaust fan must also be provided, otherwise the dust and fluff caused by the process will hamper operative efficiency.

3) Glass windows are fitted to the hood such that the flame and fabric are both clearly visible from the outside.

4) The fabric taken for singeing is dry.

5) The temperature of the singed cloth surface is measured frequently with the help of a suitable device such as a thermocouple arrangement.

6) The Speed of the fabric is measured with a speed-monitoring device and the machine is provided with automatic fabric threading devices. It must also be borne in mind that the rate of combustion of some fibres is greater than that of others. For example, the combustion of cellulose fibres is considerably quicker than that of protein fibre fabrics. Suitable adjustments must be made to the flame size and machine speed for the inflammable fibres.

Novel Singeing Method- Indirect Singeing System

Various problems are associated with direct singeing methods (e.g. gas-singeing) like uneven fame heights, clogged flame jets, slack and wavy selvedges, uneven surfaces, creases and surface flaws in the fabrics and reduced tear strength of the singed fabrics. These defects can be avoided by the indirect singeing system.

In this system hot radiation from a ceramic heat retention zone burns away the fibre protrusions. The heat is in the form of diffused infra-red radiations. This system produces more even singeing effects than those described above and can be used for fabrics having wavy selvedges. Fabrics normally singed Shirting and suiting material, sarees, dress-wear fabric, voile cloth, poplin, polyester cotton-blended fabric, etc.

Yarn singeing

Yarn meant for specific purposes such as knitting or for use as threads is also singed. The singeing in this case is also referred to as 'gassing' and the singed yarn as gassed yarn

Though fabric singeing is very much a part of a textile chemical process house, yarn singeing is not usually a process included in the chemical process house. Yarn is 'gassed' in the winding or hank-reeling department, as an operation prior to the chemical processing of yarn, in hank or cone form.

Yarns typically singed

1. Combed cotton yarn

2. Highly-twisted voile thread

3. Sewing thread

4. Polyester cotton blended yarn

5. Hosiery yarn meant for knitting.
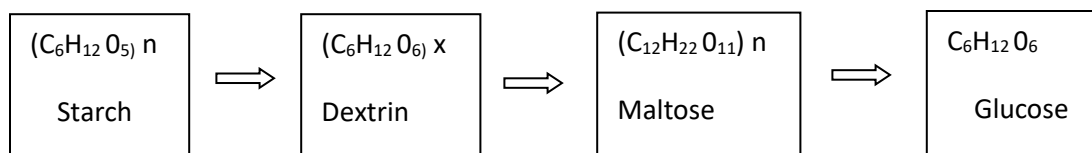
UNIT – II
DESIZING

Introduction

Grey cotton fabric contains natural impurities as well as 'size' added to the fabric to facilitate weaving. The size is added to grey fabric in a weaving preparatory process called 'sizing'. The added matter or size is removed from the fabric by a process called 'desizing'.

Sizing components such as starch, thin-boiling starch, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), vegetable oils, mutton tallow, etc., applied to cotton warp yarn to strengthen it before weaving, make the fabric unsuitable for dyeing. Although the sizing of warp is a necessary operation to the weaver, the size in the grey fabric is a hindrance to the chemical processors. Hence this unwanted size has to be removed for successful wet processing.

0bject of desizing

The object of desizing is to remove size that is applied to the grey fabric as a part of the weaving process so that the fabric becomes free of the added matter and can be effectively scoured and bleached.

Chemically, the most common constituent of size, i.e. starch is poly-$\propto$-glucopyranose, in which both straight-chain and branched-chain polymers are present. Both of these polymer types are insoluble in water but they can be solubilized by the hydrolysis of these long chain compounds to shorter ones. Thus, under suitable conditions, starch can be progressively hydrolyzed or broken down. The stages of hydrolysis are as shown below:

$(C_6H_{12}O_{5})n$	$\Rightarrow$	$(C_6H_{12}O_{6)}x$	$\Rightarrow$	$(C_{12}H_{22}O_{11})n$	$\Rightarrow$	$C_6H_{12}O_6$
Starch		Dextrin		Maltose		Glucose

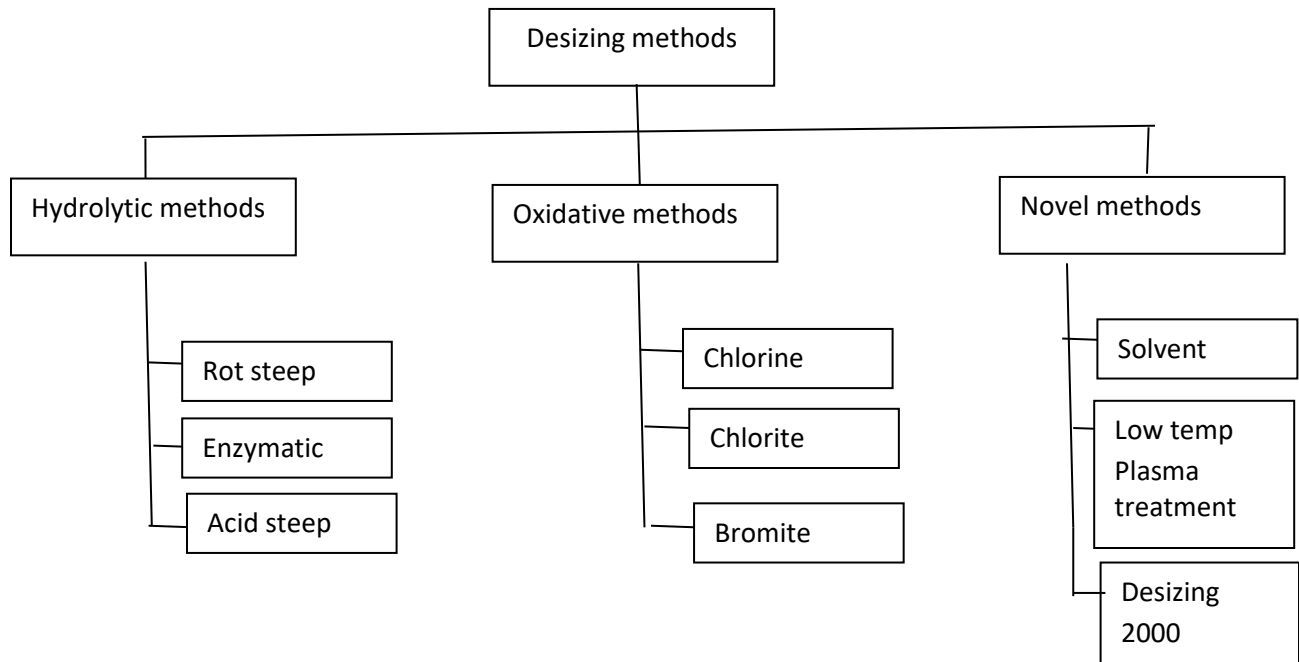**(high molecular weight) (low molecular weight)**

In desizing, the hydrolysis is carried out up to the soluble dextrin stage.

Desizing is a chemical process and its rate can be controlled. For example, if the desizing liquor is strong, the process will be completed in a short time and desizing can be carried out in a continuous manner. If relatively weak solutions are used, the process will take longer, and desizing would then necessarily be a batch process.

Since the size mixture usually contains other ingredients for which the starch acts as a binder, most of them are readily released and removed when the starch is hydrolyzed and washed off. For efficient sizing operation, the added matter is chosen such that 85 to 90% of the size should be removed during desizing. Desizing should be done uniformly. Non-uniform desizing will give uneven scouring and bleaching and hence irregular dyeing, printing or finishing.
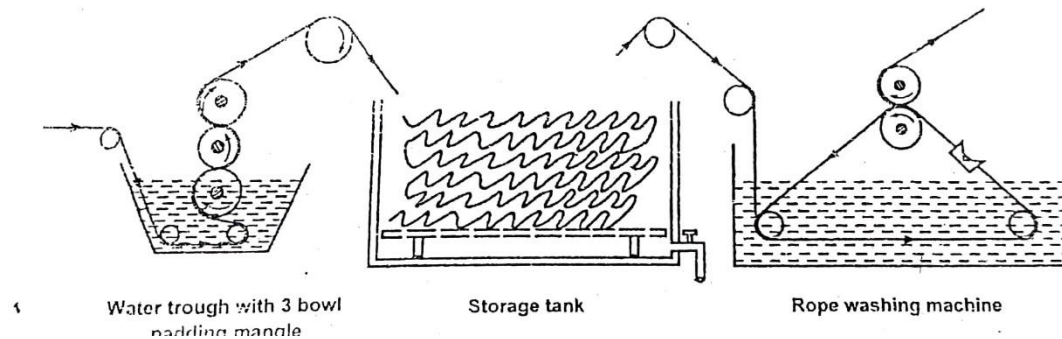
Methods of Desizing

The methods of desizing may be classified as follows:

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                        ┌──────────────────┐
                        │ Desizing methods │
                        └──────────────────┘
           ┌───────────────────┼──────────────────────┐
  ┌──────────────────┐  ┌──────────────────┐   ┌──────────────────┐
  │ Hydrolytic methods│  │ Oxidative methods│   │   Novel methods  │
  └──────────────────┘  └──────────────────┘   └──────────────────┘
        ┌──────────┐          ┌──────────┐            ┌──────────┐
        │ Rot steep│          │ Chlorine │            │ Solvent  │
        └──────────┘          └──────────┘            └──────────┘
        ┌──────────┐          ┌──────────┐            ┌──────────┐
        │ Enzymatic│          │ Chlorite │            │ Low temp │
        └──────────┘          └──────────┘            │ Plasma   │
        ┌──────────┐          ┌──────────┐            │ treatment│
        │ Acid steep│         │ Bromite  │            └──────────┘
        └──────────┘          └──────────┘            ┌──────────┐
                                                      │ Desizing │
                                                      │ 2000     │
                                                      └──────────┘
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Rot Steep

This is the oldest and the cheapest method of desizing. Here no special chemical is used. The cloth is first immersed in warm water at 40°C and then immediately passed through a padding mangle to give 100% expression. This only means that the mangle pressure is adjusted such that the cloth is squeezed to retain 100% of its weight of water. The cloth is then piled in a tank and allowed to stand for 24 hours. The microorganisms, naturally present in water, multiply and secrete starch-liquefying enzymes, which hydrolyses the starch present in the size. The cloth is finally washed with water, when most of the starch is removed from the fabric.

The actual process here is one of "fermentation' and care must be taken during rot steeping that the fermentation is not too active, otherwise the cellulose itself may be attacked and weakened. The basic steps in desizing textile fabric are depicted in Figure

Water trough with 3 bowl padding mangle   Storage tank   Rope washing machine
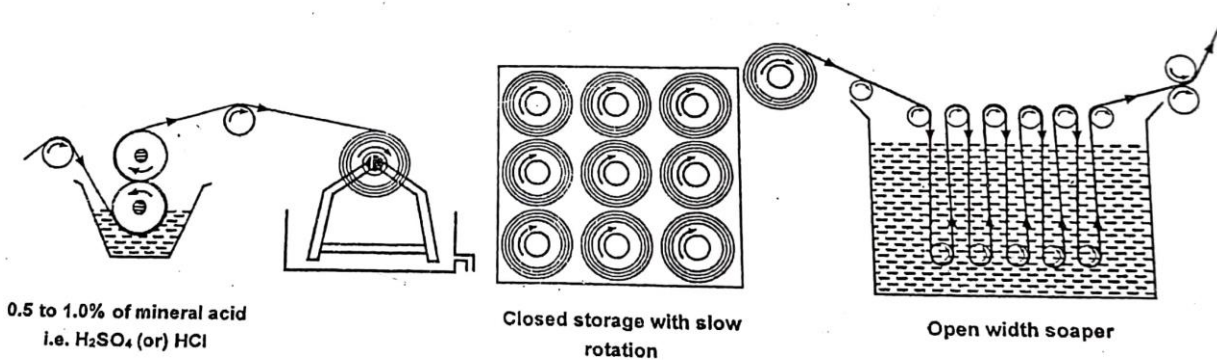
Rot Steeping

Advantages

a) Rot steeping is by lar the most economical of all desizing methods

b) It requires no chemicals.

Disadvantages

a) This process requires a large floor space.

b) It is a slow process of desizing, involving several hours.

c) There is a danger of mildew attacking and weakening the cloth if the steeping is not properly monitored.

Acid Desizing

Acid desizing involves the use of dilute sulphuric acid or hydrochloric acid. The acid hydrolyses the starch present in the sized fabric. At least a 0.2% (w/v) solution of the acid. (i.e. containing 0.2 kg of the acid for every 100 liters of the solution, at room temperature (30°C), is sufficient for this process. The cloth is impregnated with the dilute solution in a two-bowl or three-bowl padding mangle as shown in Figure.

0.5 to 1.0% of mineral acid i.e. H_2SO_4 (or) HCl   Closed storage with slow rotation   Open width soaper

The acid-impregnated fabric is squeezed evenly in the mangle and is batched wet on a roller. The wet roll is covered with polyethene film and kept aside in a room with the roll rotating slowly, so that it remains uniformly wet during the desizing action. After the prescribed period of storage, which may range from I -2 hours depending on the type of fabric and amount of size in it, the fabric is washed in an open-width soaper till free from acid and products of hydrolysis of the size ingredients. Care is taken to ensure that the acid-treated wet roll of fabric is, covered properly and kept rotating during the intermediate storage step. If any part of the fabric dries up before washing hydrocellulose will be formed and the cloth will be "tendered' (weakened).

Recipe

Mineral acid 0.5 to 1.0%

Temperature 30°C

An economical alternative to the above process is to simply immerse the fabric to be desized in rope form in the acid in a large tank and cover it with a clean, heavy fabric and a sheet of polythene film.

Special precautions are taken to ensure that no part of the process fabric is exposed to the surrounding air. As the hydrolysis of starch is an exothermic reaction, the temperature of the cloth rises, sometimes up to about 50°C, as the reaction proceeds. In a closed environment, weak mineral acid at this temperature will not hydrolyze cotton cellulose and there is no danger of the fabric 'tendering' due to the desizing process. However, if the acid-impregnated material is not closed properly, local evaporation of water from the liquor will take place, especially at places that are open to the outside air. The concentration of the acid in the cloth at such places will increase, and if the acid is concentrated to a sufficiently high value, the cellulose in the fabric will also be hydrolysed. The cloth will thus be weakened at certain places in a random manner causing uneven degradation. This damage is usually detected much later, during dyeing or printing, when uneven dyeing shows up.

 After 2-3 hours the fabric is washed in a rope washing machine till it is free of acid.

Advantages of acid desizing

a) The process is economical.

b) It is quicker than rot steeping. acid of the

c) It does not require specific conditions of temperature and pH and can be done at room temperature.

Disadvantages

The major disadvantage of the process is that care must be taken to prevent tendering of the fabric.

Enzyme Desizing

In enzymatic desizing, enzymes liquefy starch in the fabric, an enzyme is essentially a protein produced by living cells. It acts as a catalyst in chemical reactions. In almost all instances, enzymes are very specific in action, i.e. each enzyme catalyses only one reaction or type of reaction. Desizing enzymes may be classified on the basis of the source from which they are obtained as follows.

Classification of desizing enzymes

There are mainly two kinds of desizing enzymes. One type is derived from animal sources and the other from vegetable sources. The vegetable enzymes can be further classified as malt extracts and bacterial enzymes. The following table provides examples of these enzymes.

Animal	Vegetable	
	Malt extracts	Bacterial
Examples	Examples	Examples
Viveral	Diastafore	Raddase
Novofermosal	Diastase	Bidlase
Degomma	Maltostase	Taka
Slaughter house wastes, like pancreas, clotted blood, liver, etc.		Acry

The outstanding feature of the process is the specific nature of the action of the enzymes, which are active under certain conditions of concentration, pH and temperature. The optimum concentration, temperature and pH at which different enzymes are effective as desizing agents are given below:

Enzyme	Concentration (g/l)	Temperature (°C)	pH
Malt extracts	3 -20	50 -60	6-7.5
Pancreatic	1-3	50-60	6.5-7.5
Bacterial	0.5-1	60-70	5.5-7.5

Enzymes suffer from the disadvantage that if the conditions of temperature and pH are not maintained, little or no desizing takes place.

Oxidative Desizing

In this type of desizing, starch is degraded with the help of oxidation process. It is done in three ways that are, chlorine, chlorite, sodium Bromite Desizing.

Starch (Oxidation) – Soluble Products

1. Chlorine Desizing

In this process, grey fabric is padded and passed through a chamber in which gaseous medium is blown at constant concentration. Here chlorine gas reacts with wet fabric moisture and produce hydro chloric acid with releasing Nascent Oxygen.

$CL_2 + H_2O \rightarrow 2HCL + O$ **(Nascent oxygen)**
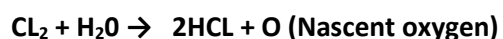
This nascent oxygen reacts with starch and make it water soluble and after the hot wash theses soluble starch is removed from the fabric.

2. Chlorite Desizing

Basically, it is used for desizing of polyester/ cotton Blend fabric. In which sodium chlorite is included in the liquor for the activation of the enzymes. The conditions for the padding liquor temperature and pH must be checked during padding.

$2NaOCL + 2H_2O \rightarrow 2\ NaOH + 2HOCL$ **(hypo chloric acid)**

$2HOCL \rightarrow 2HCL + 2O$ **(Nascent Oxygen)**
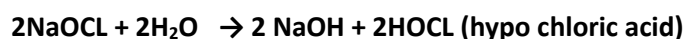
meanwhile after padding the fabric, it is kept in rotation at slow speed for 6 to 12 hrs. at ambient temperature.

3. Sodium Bromite Desizing

Sodium Bromite (3 to 5 gpl) is an oxidising agent and rapidly oxidise starch. After padding the fabric is then treated with a boil for soaping purpose. A rapid action of oxidation is sometimes harmful for the fabric. In the oxidation desizing, the chance of the damage of the cellulose is very high if it is not taken place in prescribed manner. Hence its use for desizing is very rare in textile industries. The main point of the oxidizing agent is that it can be applicable in very wider range without having any awareness of the size content. Apart from these, Alkali steeping is also done. In this method fabric is treated with 0.4-0.6% caustic soda (NaOH) solution at 60^0C to 70^0C temperature and stored for 8 to 10 hours. After this the fabric is washed and degraded starch is removed from the surface of the fabric. Some-times only hot water is also used for the desizing purpose.

Finally, a uniform Desized fabric gives good result in finishing, dyeing as well as printing department.

Novel Desizing Techniques

Other than the conventional desizing methods, various novel methods have emerged. These include, solvent desizing, low- temperature plasma treatment and 'desizing 2000.

1. Solvent desizing

Desizing can also be carried out by using some solvents (as they easily wet the fabric). The solvents are recoverable and hardly any or no effluent is discharged. This method gives a soft and lustrous feel to synthetic fibres like acrylics. This method is useful since energy consumption is low, desizing time is low and the floor space area required is less.

2. Low-temperature plasma treatment

LOW-temperature plasma treatment is an eco-friendly process wherein the fabric to be desized is exposed to plasma generated by special equipment, in specially evacuated chambers. The extent of size removal depends on the radio frequency applied in the process, dwell time of the treatment and the plasma-gas composition.

3. Desizing 2000

This is a simple and reliable combined desizing and demineralization process of cotton with only three auxiliaries, viz. Beixon NE, Kollaso IMCE and Beisol T2090 by cold pad-batch or pad-steam process.

Assessment of desizing efficiency

Industrially, the assessment of desizing process efficiency is done by rating the process on a TEGEWA violet scale

TEGEWA agent is basically a diluted solution of iodine in water and alcohol. When this solution is applied on a desized fabric, the iodine in solution reacts with residual starch in the fabric and forms starch iodide. This is blue in colour and the intensity of colour indicates amount of residual starch on fabric. The lesser the intensity of colour, the higher the starch removal and higher the TEGEWA rating of the fabric.

Reagent preparation

Put potassium iodide [10g of KI (100%)] in 100 ml of water; then add 0.6358 g of iodine (100%); stir well until iodine is completely dissolved in the KI solution. After this, add 800 ml of ethanol. Then by adding water the volume should be raised to 1000 ml.

Method of testing

Put one or two drops of the above solution on a fabric. Rub it gently and then assess the colour change as per the Tegewa scale. Before testing, the fabric should be cold and there should not be any residual alkalinity in it.
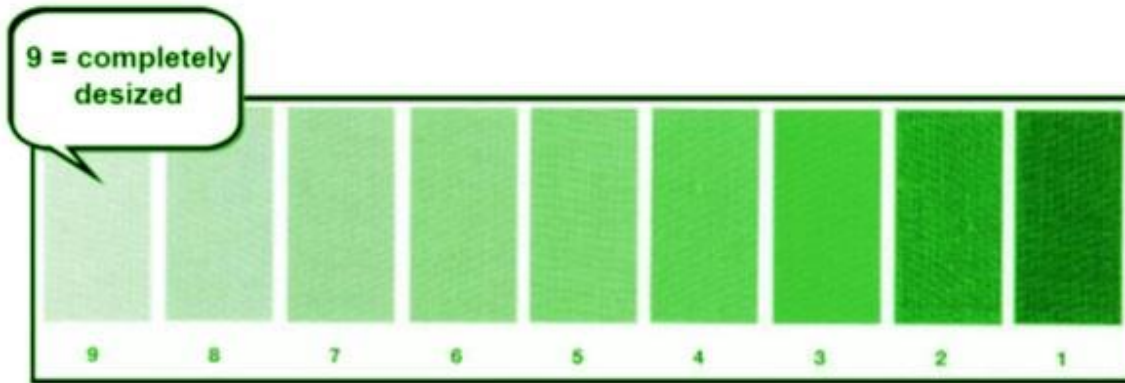
Assessment

No Colour Change = No starch is present

Pale blue to bluish violet = Presence of starch size or a blend of starch+ synthetic size

Brown = Presence of modified starch or a blend of starch/PVA size

TEGEWA violet scale (1-9 from right to left)

Complete removal of starch will not result in any colour formation (rating – 9) and poor starch removal can give intense blue colour (rating – 1).

UNIT- III

SCOURING

Introduction

After desizing, the cloth is free of much of the substances added by man during weaving, but it still contains natural impurities like oils, fats, waxes and colouring matter, remnants of the added matter, adventitious dirt and/or stains.

The oils and fats are higher fatty acids of inorganic compounds. They are hydrophobic (water-hating) substances and affect the absorbency of the cloth. They form a thin layer on the fibre surface that resists the penetration of water. In this state therefore, the cloth cannot be dyed or printed. The outer hydrophobic layer has to be removed to make the fabric absorbent. The process by which this water-resistant layer is removed from the fabric is called 'scouring'

Table 1.1 gives a list of the constituents in dry cotton fibre.

Table 1.1 Constituents of dry cotton fibre

Components	Percent by. Weight
Cellulose	94.0
Protein	1.3
Ash	1.2
Oil and wax	0.6
Sugar and pigment	0.3
Other substances	2.6

In cotton textile processing, scouring is also referred to as kiering, kier-boiling or boiling-out as the process involves boiling the cloth or yarn in alkaline chemicals. The boiler or vessel in which this is done is called a 'kier 'and hence the terms kiering and kier-boiling.

Objects of Scouring

The objects of scouring are twofold:

i) To remove natural as well as added impurities of essentially hydrophobic character (oils, fats, waxes, etc.) as completely as possible and leave the fabric in a highly absorptive condition without undergoing significant chemical or physical damage

ii) To make the goods suitable for removing the natural colouring matter of the cotton during the subsequent bleaching process.
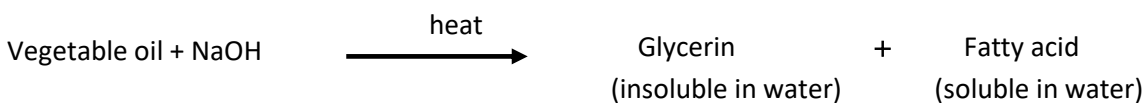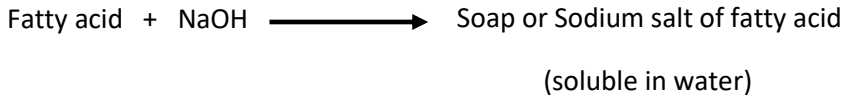
Changes Taking Place During Scouring

During the scouring process the following changes take place in the outer hydrophobic layer of the fibre:

    I.   The saponifiable oils in it are converted into soaps.

   II.   The unsaponifiable oils and waxes it contains are emulsified.

  III.   The proteins are hydrolysed into soluble products.

  IV.   The pectose and pectin are changed into soluble salts of pectic or metapectic acid.

   V.   v)Simpler amino-compounds are dissolved or hydrolysed to ammonia.

  VI.   Mineral matter is dissolved.

 VII.   Dirt particles are removed and held in a stable form in the kier liquor.

Saponification

Vegetable oils, animal fats and mineral oils are not soluble in water. A vegetable oil is a glyceride of fatty acids like oleic, stearic and palmitic acids. When oil is heated with a solution of sodium hydroxide in water, the oil is split up into its constituents, namely fatty acid and glycerin. The glycerin dissolves freely in water. The fatty acid reacts with the sodium hydroxide present in the solution to form its sodium salt i.e. soap, which is also soluble in water. Conversion of glycerides of fatty acids into soap by the use of sodium hydroxide is called 'saponification, Thus the oils and fats in the cotton textile are saponified during the scouring process into water-soluble products.

$$\text{Vegetable oil + NaOH} \xrightarrow{\text{heat}} \underset{\text{(insoluble in water)}}{\text{Glycerin}} + \underset{\text{(soluble in water)}}{\text{Fatty acid}}$$

Fatty acid + NaOH $\longrightarrow$ Soap or Sodium salt of fatty acid

(soluble in water)

Emulsification

Any waxes present in the fibre cannot be removed by saponification. Waxes are esters of higher fatty alcohols and fatty acids. They are hydrophobic in character. They can however be removed from the fibre by converting them into emulsions, which can be held in the kier liquor. An emulsion is a fairly stable mixture of two liquids, which do not mix with each other. The soap formed by the saponification of oils in the kier acts as the emulsifying agent. In addition to this, soap is also added separately to the kier liquor along with the other scouring chemicals.

Waxes+ Soap (already formed by saponification or added) $\longrightarrow$ Suspension or emulsion
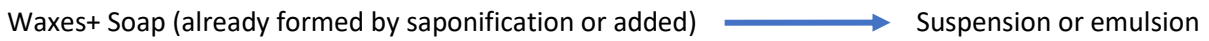
Chemicals Used for Scouring

Detergents

When impurities of adhesive nature, e.g., oils, fats, etc., are removed, the dust and dirt deposited on the textile material during handling and other constituents of size, e.g. china clay, get loosened and try to leave the fabric especially under elevated temperature and pressure. These impurities are dispersed in the scouring liquor and are likely to get deposited back on the material. To prevent this, a detergent is added to the scouring liquor to keep the solid particles suspended in the solution and prevent them from settling on the fabric. All good detergents are also good wetting agents. (But all good wetting agents need not be good detergents.)

Surfactants (wetting agents)

The surface tension of water prevents the wetting of hydrophobic material and it is therefore necessary to reduce it to enable fabric to be wetted easily. Substances that reduce the surface tension of water are termed as surface-active agents or briefly as Surfactants. Since they facilitate the phenomenon of wetting, they are also referred to as wetting agents. For satisfactory removal of impurities during scouring it is necessary to incorporate a wetting agent. When a good detergent is used in the scouring liquor, the addition of wetting agent may not be required.

Methods of Scouring Used for Common Fibres

As textile fibres vary from one to another with regard to physical and chemical properties, a variety of scouring processes are used. Further, the process used will also depend upon whether the textile

material is handled in loose fîbre, yarn or fabric form. Yet again, the scouring of blended textiles will require processes that are compatible with the fibres constituting the blend.

Large batches of cotton textiles, particularly yarn and fabric, are predominantly Scoured in kiers, which are thick-walled metal vessels having provision for heating the textile material and the scouring chemicals under pressure.
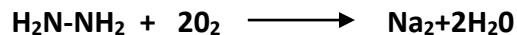
Kiers

Some kiers are vertical while others are horizontal. Vertical kiers are sometimes used closed and sometimes open. Depending on the methods of heating used, kiers are divided into three types, namely,

1. Those heated by direct steam within the kier

2. Those heated by indirect steam (closed-coil) within the kier and

3. Those heated by indirect steam outside the kier.

Kiers heated by direct steam within the kier

In the first type, the rate of heat transfer from the steam to the liquor is a maximum because of its direct contact but there is condensation of a part of the steam, which dilutes the liquor and also increases the volume of the liquor, generating hydraulic pressure. Steam also brings with it some amount of air (oxygen), which was dissolved in the water. This oxygen degrades cotton under the scouring conditions. Hence hydrazine ($H_2N=NH_2$) is added to the water to consume the dissolved oxygen as follows:

$$H_2N\text{-}NH_2 \ + \ 2O_2 \longrightarrow Na_2 + 2H_2O$$

Kiers heated by indirect steam (closed-coil) from within

In this type of kier, the liquor is heated with closed steam coils inside the kier and therefore the efficiency of heat transfer is lower than that in the first type but there is no dilution of the liquor or increase in its volume or the hydraulic pressure.

Kiers heated by indirect steam from outside

The third type of kier is similar to the second type above except that the liquor is heated outside the kier.

Kier Boiling Assistants

Several types of chemicals are used in the kier boiling of cotton textiles and each of them has a specific role to play in the scouring process. The functions of such chemicals are briefly described below.

Caustic soda

This converts the saponifiable oils and fatty acids in cotton to soluble sodium soaps; the calcium and magnesium pectates and free pectic acid are converted into soluble sodium pectates; specks and other mechanical impurities are softened.

Sodium carbonate

Fats contained in the size and those difficult to saponify may be more easily elimi- nated by soda ash.

Sodium bisulphite

Being a reducing agent, sodium bisulphite prevents any oxygen in the kier from affecting the cotton cellulose.

Sodium silicate

This chemical prevents the formation of iron stains in the fabric. The iron comes from ferric hydroxide, which is contained in water of high iron content. It also contributes to the whiteness of scoured fabric by absorbing the products of decomposition of the natural impurities in cotton.

Sodium hexa-meta-phosphate

This chemical is added to the kier to reduce the hardness of water

Sequestering agent

 A sequestering agent can "chelate (combine to form complexes with) the metallic ions in water and also reduce the hardness of water. These agents can replace the use of sodium silicate and sodium hexa-meta-phosphate to some extent.

Surfactants (mainly wetting agents)

The term surfactant is a short form of 'surface active agent'. Surfactants possess wetting, emulsifying and detergent properties. They facilitate penetration of the solution into the fibre and rapidly emulsify wax-like substances.
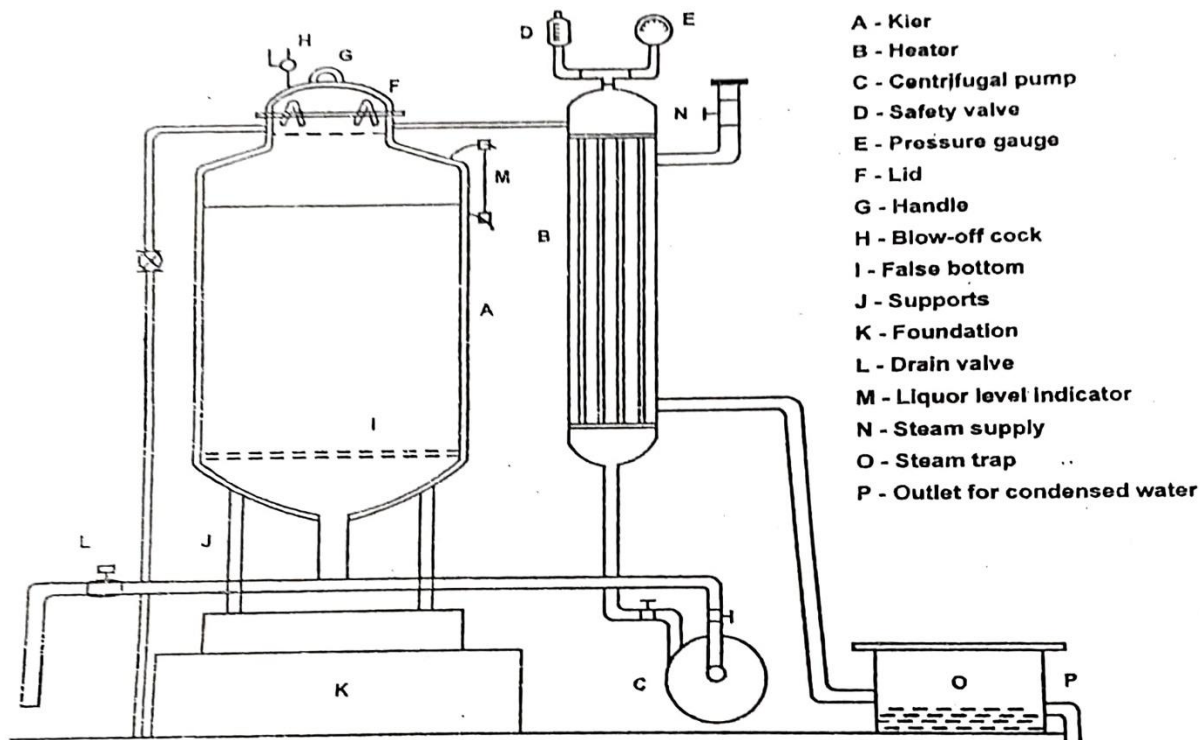
Oxidizing agents

Sodium hypochlorite or hydrogen peroxide further disintegrate the decomposition products of the impurities in cotton and as a result the time of scouring is reduced and better whiteness and wettability are imparted to the material.

Description and Working of a Kier

I. A kier is a cylindrical vessel, generally vertical, capable of holding I to 3 tons of cloth.

II. A 2-tonne kier, having dimensions of 2.7 m (or about 9 feet) in height and 1.95 m (or about 6% feet) in diameter, is commonly used for boiling.

III. Horizontal kiers have also been in use.

IV. Kiers are made of mild steel plates, 0.6 cm thick. joined by welding or riveting.

V. They are provided with a pressure gauge and a safety valve.

VI. High-pressure kiers have a hole at the top through which cloth is introduced or removed.

VII. As the kier is made of iron, a lime wash (i.e. painting with a mixture of lime, cement and sodium silicate) is given to its inner wall to avoid the formation of rust stains on the cloth when it comes in contact with the inner wall of the kier.

Figure. shows the essential parts of a vertical kier. Kiers are used as pressure kiers or as open kiers. When the lid of the kier is removed or opened, it serves as an open kier working at atmospheric pressure.

A - Kier
B - Heater
C - Centrifugal pump
D - Safety valve
E - Pressure gauge
F - Lid
G - Handle
H - Blow-off cock
I - False bottom
J - Supports
K - Foundation
L - Drain valve
M - Liquor level indicator
N - Steam supply
O - Steam trap
P - Outlet for condensed water

(VERTICAL KIER)

Loading the kier

I.   The grey fabric, after desizing, is loaded into the kier in rope form' by piling it uniformly either by means of an automatic piler or by manual piling.

II.   When the selvedges of a running fabric are brought together and the fabric assumes the shape of a thick 'rope-like' continuous strand, it is said to be in rope form. This is generally achieved by passing a wet fabric in open-width form through a 'pot-hole' shaped stainless steel or porcelain ring of appropriate size.

III.   With manual piling, it is possible to load about 80% of the kier capacity whereas with an automatic piler (which is used in modem kiers) only about 70% of the capacity used.

IV.   The kier should not be filled beyond 80 to 85% of its rated capacity overfilling may create undue hydraulic pressure and would also compress the fabric at the top of the kier and hinder the circulation of the liquor, thereby increasing the temperature gradient between the top and bottom of the kier.

V.   Conversely too, small quantities of material, very much below the capacity of the kier, should not be boiled in a large kier; the kier should be at least half full; otherwise the cloth may turn around due to the circulating liquor and get hopelessly entangled.

VI.   It is most important to ensure even and regular packing of the goods, be it fabric or yarn, in the kier. Only then will the scouring liquor be able to pass evenly through the material.

VII.   Uneven piling will cause "channeling', i.e. passage of liquor very easily through loosely packed material.

VIII. It is obvious that in the event of uneven distribution of tightly packed and loosely packed material, the liquor will choose the path of least resistance, i.e. through the latter. Consequently, there will be little or inadequate flow of liquor through the former.

IX.   This would ultimately result in uneven scouring; the tightly packed material being scoured only partially. Unevenly scoured textiles will bleach and dye unevenly.

X.   When scouring yarn in hank form in a kier, there are two ways of handling the yarn. one, the hanks are linked together by short lengths of cotton twine to form a continuous chain of hanks that is convenient to handle as a long 'rope'. Another way of doing it is to prepare small, loosely tied bundles of the hanks and pile them evenly in the kier.

XI.   After the material is piled in the kier, heavy stones are placed uniformly on it to prevent it from being tossed up during boiling and thereby forming channels, which, as explained above, would lead to uneven scouring results.

XII.   Clean jute cloth or cotton sheeting may be placed between the material and the stones. Before entering the kier, the cloth may be impregnated with alkaline liquor in a trough and mangled to ensure even treatment of the cloth.

Removal of air from the kier

I.   After loading the fabric, the kier liquor is let in from the bottom of the kier to sweep out the air inside. The M:L ratio in a kier is usually 1:4 or 1:5.

II.   The term 'material-to-liquor ratio' or M:L ratio is used frequently in textile wet processing and is a ratio relating the dry weight of the textile material being wet processed to the total volume of treatment liquor.

III.   For example, a material to liquor ratio of 1:5 simply means that 5 liters of treatment liquor are available for every kilogram of the dry textile material. Obviously, this is the same as saying that 5 ml of liquor are available for every gram of the material.

IV.   There should be enough kier liquor for efficient circulation by a pump.

V.   The liquor coming into the kier brings with it air, which if allowed to remain in the kier would attack the cotton cellulose forming oxycellulose. So, the air has to be removed.

VI.   This is achieved by heating up the liquor, then closing the kier with the lid and allowing the air to come out of the air valve over the lid.

VII.   When direct steam is turned on, the liquor boils and expels the dissolved air. Subsequently the direct steam is stopped and the air valve is closed. Only a part of the air is removed this way.

VIII.   For satisfactory removal of air, the liquor should be circulated for 15 minutes and the circulation stopped and restarted when the kier liquor starts coming out from the air valve.

IX.   Complete immersion of the material and the removal of air are most essential in order to prevent formation of oxycellulose, which is rapidly produced by the action of air on cotton.

Cotton contains about 0.5% oils and waxes that have to be removed by scouring. For kier boiling cotton, a mixture of 1 to 1.5% caustic soda solution, 1% sodium silicate and 1% soap on the weight of the material is typically used. Boiling under a pressure of 1.5 to 2.0 kg/cm^2 (22 to 30 lb/inch^2) for 6 to 10 hours is adequate for most goods but this varies depending on the type of fabric. Most goods, which are to be sold in the white state, are boiled twice, first with sodium hydroxide and then with sodium

carbonate. It normally takes two hours for the liquor to reach the required pressure in a kier and a kier boiling cycle could take from 6 to 12 hours depending upon the capacity of the kier.

Recipe and conditions for cotton scouring

Sodium hydroxide -1 to 1.5%

Sodium silicate 1% Soap 1%.

Detergent (wetting agent) -1%

M:L ratio -1:5

pH 10 to 11

Pressure -1.5 to 2 kg/cm*

Time -6 to 12 hours

Scouring of Natural Polyamide or Protein Fibres (Silk and Wool)

Scouring of wool

I. The scouring of wool differs from cotton in two essential respects.

II. Firstly, raw wool contains anything from 30 to 60% of wool grease, compared with 0.5% of oil and wax in cotton.

III. Secondly, wool is very rapidly degraded by alkali so that if the natural oils and fats are to be saponified, the alkali must be applied with caution and at temperatures well below the boil.

IV. In practice, sodium hydroxide is never used because the slightest excess would raise the pH above the danger level, and milder alkalis such as sodium carbonate and ammonia or ammonium carbonate are preferred.
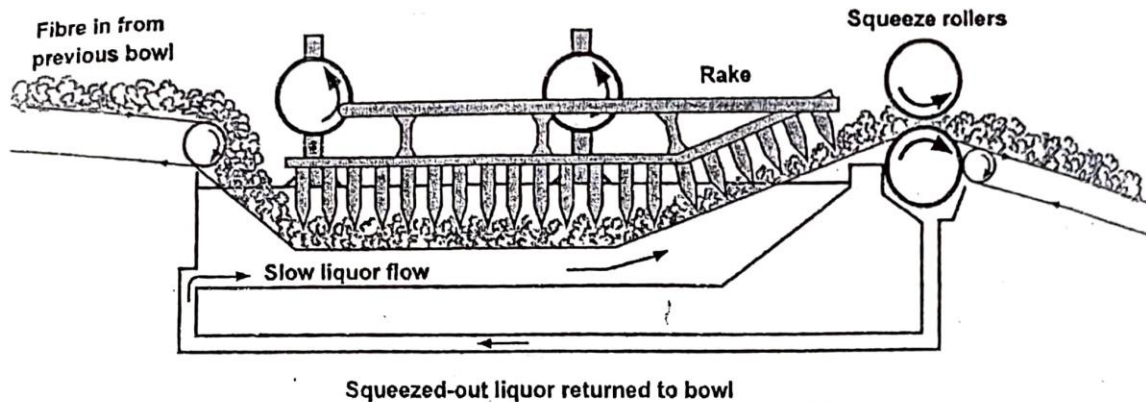
(SCOURING OF WOOL)

Raw wool is, scoured by the **counter-current method**.

I. There are generally either four or five bowls, similar to the one illustrated in Figure 1.11, arranged in sequence so Wool passes directly out of the first and into the second, and so on.

II. The machine consists essentially of a long trough provided with rakes, a false bottom, and at the exit, a wringer.

III. Below the false bottom is a spirally fluted shaft which, when it rotates, carries the deposited solid dirt to the center where there is an outlet valve through which it can be discharged.

IV. The trough is filled with scouring liquor, containing soap and sodium carbonate, and the temperature is brought to 35 to 40°C.

V. The rakes have a reciprocating movement that makes the wool travel forward beneath the surface of the liquor whilst adequate agitation is maintained to keep the dirt and emulsified grease in suspension.

VI. As the wool leaves the trough, the excess of soap liquor is squeezed back by the wringer's, the wool passing to a second, similar trough, where it usually receives further scouring, since removal of impurities will not be complete in the first.

VII. This may be repeated two, three, or four times before the wool passes through a final trough where it is rinsed with water.

VIII. The amount of alkali added should never be so much as to bring the pH above 10.

The composition of the scouring liquors varies considerably according to local practice. The following concentrations are typically used for bowls of about 7000 liters capacity each.

Soap

First bowl -0.75 to 0.8 %

Second bowl -0.4 to 0.5 %

Third bow -0.25 to 0.35%

Fourth bowl water only

Alkali (sodium carbonate)

First bowl 0.2%

Temperature 30 to 40°C

pH 10

IX.   Scouring is carried out at 35 to 40°C and the temperature should never, under any circumstances, be allowed to exceed 60°C because of the risk of degradation of the wool keratin by the alkali.

X.   The soaps selected for the process must be made of fatty Acids and have low melting points, only then will they be more soluble at lower temperatures, and also because they will be more easily rinsed out.

XI.   When two or more bowls are scouring in sequence, the counter-flow system is generally used.

XII.   This means simply that as the wool emerges from a trough the wringers squeeze the excess liquor into a receptacle connected to the preceding bath : Thus there is a gradual transference of liquor from the last to the first compartment, the flow being in the opposite direction to that in which the wool is travelling.

XIII.   Fresh soap and alkali are fed into the last tank so that the wool that is virtually grease-free receives the most effective detergent treatment, and the dirtiest wool, which easily parts with the bulk of its grease, meets the partly-spent liquor, which is ultimately discharged from the first trough.

XIV.   Whilst the bulk of detergent can be fed into the last bowl some replenishment of the others is usually necessary.

Other methods of scouring wool are:

1. Solvent scouring

2. Freezing method

3. Emulsion scouring.

Degumming of silk

I.   Degumming of silk presents special features because it is usually accompanied by the removal of the silk gum or sericin.

II.   The process is commonly referred to as boiling off".

III.   Silk is scoured to different extents depending upon the specific kind of Silk required.

IV.   Souple silk is raw silk from which about 10 percent of the gum has been removed, and in ecru only about four percent is taken away, the object being to cleanse the silk rather than to degum it.

V.   The boiling off, which depends upon the solubility of sericin in hot soap solution, and any mild alkali sometimes added, is the same for complete degumming, souple or ecru, but differing only in the time of treatment.

VI.   Degumming is carried out by treating the silk for two hours, or more if necessary, at about 95°C in a 0.5 to 0.75 percent solution of soap, using 30 liters of liquor per kilogram of silk.

VII.   Hosiery goods are packed into mesh bags and degummed in a rotary scouring type of machine, made out of metal with extremely smooth surfaces because of the tendency of the fibres to rupture.

VIII.   Hanks of yarn can be packed into bags and degummed in an annular-cage forced-circulation machine, but they are also frequently hung-over sticks and boiled off in an open bath, movement being provided by manual turning.

IX.   The solubility of sericin in soap depends upon the alkalinity produced by hydrolysis, and for this reason the synthetic detergents are not so good.

X. It has been demonstrated that silk can be degummed with a mixture of sodium carbonate and sodium bicarbonate, the concentration and proportions being adjusted to maintain the pH of the liquor at 10.

XI. Although it costs less the process has not found much favor because soap gives a better handle.

XII. Vigorous movement, contact with rough surfaces, and exposure to mechanical stresses and strains are undesirable at all times during degumming, but especially when sodium carbonate has been added to the liquor.

XIII. Under such circumstances the fibroin filament ruptures, and bundles of the fibrils of which it is composed project from the surface giving 'lousy silk.

Degumming recipe

Soap solution 0.5 to 0.75%

Temperature -95°C

Time -2 hours

M:L ratio 1:30

Scouring of Man-made Fibres

I. The man-made fibres are comparatively free from impurities and much milder methods of scouring are therefore sufficient.

II. The **regenerated celluloses** have poor wet strength, unless they are the highly-oriented varieties, and mechanical handling must be gentle.

III. Fabrics should be scoured in stainless-steel winch machines, and not in machines with heavy rollers such as those used for wool.

IV. The roughness of a wooden machine is liable to cause rupturing of the threads by plucking them in their weak wet state.

V. **Rayon yarns** are scoured in a hank or package-dyeing machine. **Regenerated rayon** is scoured at 80 to 90°C with a 0.3% solution of soap or a synthetic detergent. Up to 1% of the weight of the goods of sodium carbonate may be added, but this is rarely necessary.

100% rayon fabric may be scoured using the following recipe

Recipe

Soda ash 1 to 2 g/l
Detergent 1 to 2 g/1
Temperature 60 to 70°C
Time 30 minutes

VI. Greater care must be taken when scouring **cellulose acetates**.

VII. If alkali be present and the temperature exceeds 75°C the fiber commences to hydrolyse, the outermost layers of the fibre become converted to cellulose, which causes a reduction of lustre and an alteration in the dyeing properties.

VIII. Since soap solutions themselves are slightly alkaline, the temperature during scouring should, even in the absence of alkali. not exceed 85°C.

IX. The risk is less with synthetic detergents since they do not hydrolyse with the liberation of hydroxyl ions as does soap.

X. Cellulose acetate becomes somewhat thermoplastic when in a hot wet state. If, under such conditions, it is allowed to lie in folds, especially when the weight of a pile of fabric presses on the fold, a permanent crease is liable to be formed.

XI. For this reason, it is desirable to use long shallow machines with elliptical winches to prevent the formation of piles, and unduly prolonged runs in a hydro-extractor should be avoided.

A typical **scouring recipe for acetate fabric** is given below.

Detergent 1 g/l

Temperature 85°C

Time 30 minutes

For **100% polyester fabric** the same recipe as that for 100% rayon fabric may be used.

For **polyester/cotton blends** the following recipes have been used.

Soda ash 0.5 to 1% (on weight of material)

Detergent 0.2 to 0.5% (on weight of material)

Temperature 100°C

Time 60 to 90 minutes

An **alternate recipe** is as follows:

Sodium hydroxide 0.2 to 0.5%
Detergent 0.2 to 0.5%
Temperature 75^{0}C
Time 60 to 90 minutes

Assessment of scouring efficiency

Degradation of Cotton during Scouring

Main changes:

- Loss in weight (5-10%)
- Significant increase in absorbency (1-3 seconds)
- Improvement is TEGEWA rating
- Slight increase in average DP (due to removal of low mol. Wt. components)
- Shrinkage

Assessment of scouring efficiency

1. Practical tests of absorbency
2. Measurements of
   (a) Weight loss
   (b) Protein content
   (c) Residual wax content
   (d) Methylene blue absorption (removal of pectic substances)

Practical tests of absorbency

Sinking time test (AATCC Test Method 17-1994).
A hank of known weight (e.g. 5 g) forming a loop of 45.7 cm is tied with a flat cylindrical plate (25 mm diameter) of small defined weight (say 15-40 g) called *sinker.* The sinker is attached to the hank with the help of a hook weighing about 3 g. It is then dropped slowly on water contained inside a glass measuring cylinder (500 ml). At first, the hank floats due to entrapped air. Slowly the hank is wetted and entrapped air is removed. The time required by the hank to go inside water from floating state is known as sinking time.

Drop test in which water drops are allowed to fall by gravity from a burette placed at a certain height from the fabric surface. The fabric is placed straight on a table without any creases. The time required

for the drops to collapse is noted as wetting time.

AATCC Test Method 27-1994 - evaluation of rewetting agents.
Although cotton is stable in dilute alkalies at high temperatures in absence of air, presence of air causes serious degradation. The degradation may be assessed by determining one or more of the following:

1. *Copper number,* a measure of the reducing groups present in cellulose.
2**. Carboxyl group** content.
3. *Cuprammonium fluidity,* which is a measure of molecular chain length of cellulose.
4. Tensile strength of the cotton material before and after scouring.

Copper number
The reducing groups present in degraded material are capable of reducing an alkaline solution of copper sulphate, when insoluble cuprous oxide is formed and deposited on the cellulose material. The amount of cuprous oxide formed is proportional to the amount of reducing groups and is expressed by Copper Number, which is defined as grams of cupric copper reduced to cuprous oxide by 100 g of cellulose under standard conditions of boiling in alkaline medium.

Copper Number= 63.5 x V X N x 100 / W x 100

Where V is the ml of ceric solution consumed after deducting blank reading, N is the normality of ceric sulphate solution and W is the weight of the bone-dry cellulose sample (0.25 g for normal samples and 0.1 g for highly degraded samples having copper number greater than 4).
The copper number of pure cellulose ~ 0.05,
For raw cotton ~ 0.9 due to the presence of impurities
Well-scoured and bleached cotton material > 0.3
For regenerated fibre should be > 1.2.

Cuprammonium fluidity
The degradation, in terms of reduction of the degree of polymerization, can also be assessed by measuring fluidity of the cotton material dissolved in cuprammonium hydroxide solution. The degree of polymerization of a polymer is directly proportional to the viscosity of its solution, providing all solutions are at the same concentration.
Unbleached cotton shows a fluidity of about two. Generally, bleached cotton with a fluidity of five or less is accepted commercially. Above a value of ten, chemical damage shows up as a loss in tensile strength. The standard unbleached viscose has a fluidity of about ten.

Physical testing
▶ Tensile strength, bursting strength and abrasion resistance, Tear strength can be measured
▶ The results are influenced by both fabric structure and chemical damage.
▶ Tear strength is also influenced by residual natural lubricants.

Staining tests

carboxyl groups in oxidised cellulose resist staining with C.I. Direct Blue 1 or give increased uptake of C.I. Basic Blue 9.

Harrison test
The oxycellulose test sample is immersed in a boiling alkaline silver nitrate solution.
Brown to black deposits of silver are produced on the substrate where there are reducing aldehyde groups.

UNIT- IV

BLEACHING

Introduction

Bleaching is a process by which the natural colouring matter and any other colouring matter is removed from natural fibers or process discoloration from man-made fibres. For example, scouring of cotton removes all of the impurities except the natural colouring matter and leaves the material satisfactorily absorbent but still grey' in colour. The natural colouring matter is of no harm to the fibre except that it diminishes fibre whiteness. If the fibre is to be dyed to very dark shades where fibre brightness is not important, no bleaching is required. However, for light and medium shades or when fibre brightness is important, bleaching becomes an essential operation before dyeing or printing. With regard to man-made fibres, which are generally white', manufacturing process sequences can cause a slight discolouration that sometimes cannot be accepted as 'full' white. In such cases bleaching is the only resort.

The natural colouring matter can be destroyed by oxidation (oxidation bleach) or by reduction (reduction bleach) or a combination of both.

Classification of Bleaching Agents

Bleaching agents can be broadly divided into two groups.

1.Oxidising bleaching agents

2. Reducing bleaching agents.

1.Oxidising bleaching agents

A list of oxidising bleaching agents is given below:

1. Chlorine (Cl_2).

2. Hydrogen peroxide (H_2O_2)

3. Sodium peroxide (Na_2O_2)

4. Potassium persulphate ($K_2S_2O_8$)

5. Hypochlorous acid (HOCl)

6. Potassium permanganate ($KMnO_4$)

7. Perborates (e.g. KBO_4)

8. Ozone (O_3)

These agents use oxygen directly or indirectly for the bleaching action. Nascent oxygen decomposes colouring matter completely into simpler compounds which can be washed away with water during washing and which do not give any trouble at a later stage.

2. Reducing bleaching agents

Some reducing type of bleaching agents that have been in use are listed below:

1. Sulphur dioxide (SO_2)

2. Sodium sulphite (Na_2SO_3)

3. Sodium hydrosulphite ($Na_2S_2O_4$)

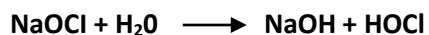4. Sulphurous acid (H_2SO_3)

5. Bisulphites (e.g. $NaHSO_3$)

In most of the reducing bleaching agents, the nascent hydrogen combines with the colouring matter in the fibre to produce a colourless compound which remains in the fabric, this generally gets oxidised back to the original colouring matter upon exposure to the air. Hence the whiteness produced by a reducing bleaching agent is not permanent.

Bleaching of Cotton with Sodium Hypochlorite

Sodium hypochlorite Sodium hypochlorite is the strongest oxidising agent because it is capable of giving Oxygen at room temperature. It is also economical in use. A study of the reactions shown below will help to understand how the bleaching action occurs.
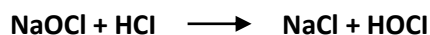
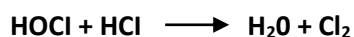Chemical reactions in hypochlorite bleaching

1. **Hydrolysis**

   $NaOCl + H_2O \longrightarrow NaOH + HOCl$

2. **Bleaching agent release**

   $HOCl \longrightarrow HCl + [O]$

3. **Max -HOCl development**

   $NaOCl + HCl \longrightarrow NaCl + HOCl$

4. **Formation of free chlorine**

   $HOCl + HCl \longrightarrow H_2O + Cl_2$

When sodium hypochlorite dissolves in water, it is hydrolysed and gives rise to hypochlorous acid (HOCl), which is unstable and dissociates to yield active oxygen. In the presence of oxidisable substances the very weak hypochlorous. acid is converted into strong hydrochloric acid (shifting pH bath). Addition of caustic soda shifts the equilibrium of Equation 1 to the left, hypochlorous acid concentration decreases, bleach bath stabilises itself and the bleaching action diminishes.

The hypochlorous ions (OCl^-) in the bleaching bath cause bleaching of natural colouring matter by oxidation. The bleaching mechanism is governed by equilibrium at different pH conditions. To avoid fibre damage and to maintain the pH in the region of 10.5 to 11, it is always advisable to include in the bleach bath a buffer of 5 -10 g/l of sodium carbonate. Sometimes a small amount of caustic soda too can act as a pH stabiliser, but frequent checks need to be done to ensure the safe hypochlorite bleaching pH conditions. Figure. illustrates this graphically.

Figure.

 The concentrations of HOCl and OCl^- ions at different pH values in a hypochlorite bleaching bath

Sodium hypochlorite bleaching

When cotton goods are to be bleached, they are scoured or kier-boiled and then uniformly packed into a cylindrical or rectangular vessel which may be made of wood, stone, cement lining or stainless steel. The vessel has a perforated false bottom with an outlet to a tank below (sump) of similar capacity. The liquid in the sump is made up to the desired concentration of available chlorine with sodium hypochlorite solution. It is then pumped up and spread, through sprinklers, over the top of the cotton goods, through which it percolates to find its way ultimately back into the sump. An arrangement of this kind is shown in Figure.

The concentration of available chlorine required in the bleach liquor varies between 1 to 3 grams of available chlorine per litre, but for most purposes good results can be obtained with concentration of 1.5 g/l of available chlorine. The time of treatment depends upon the cotton material being bleached, highly twisted yarn or close-weave fabric requiring more time. The time is also a function of the surrounding temperature, less time being required in hotter ambient temperature. A one-tonne load of cotton textile may take an average of about four hours for effective bleaching or "chemicking" to take place.

Recipe

Bleaching liquor - 1.5 g/l of available chlorine

Temperature -Room temperature

pH -10 to 11 (using a suitable buffer)

- A- Sump (Bleaching liquor)

- B- B-Perforated false bottom

C-Cloth (or) Hank yarn

D-Pump

E-Sprayer

F-Thick cover fabric

Figure. Hypochlorite bleaching

Precautions to be taken during hypochlorite bleaching

Cellulose textiles are to be bleached very carefully with hypochlorite. The four variables that affect the bleaching efficiency are,

i) Concentration of the bleaching liquor

ii) Its temperature

iii) Its pH, and

iv) The time of bleaching.

The greater the concentration of the bleach liquor, other factors remaining constant, the better the bleaching result but greater the risk of chemical damage to the cellulose. Time and temperature must also be standardised in industrial practice, to minimise chemical damage. The pH should be controlled to be between 10 and 11, a fall in pH to below 9 accelerating the degradation of the cellulose material through the formation of oxycellulose. It is therefore important to have a process control check of the concentration, pH and temperature of the hypochlorite bleach bath during industrial bleaching.

Bleaching of Cellulose Fibres with Bleaching Powder

Bleaching powder is a mixture of the basic hypochlorite $Ca(OCl)_2 2Ca(OH)_2$ and the basic calcium chloride $CaCl_2.Ca(OH)_2.H_2O$ in such proportions that the product contains roughly equimolecular amounts of calcium chloride ($CaCl_2$) and calcium hypochlorite [$Ca(OCl)_2$] together with substantial amounts of free calcium hydroxide [$Ca(OH)_2$]. The chlorine in calcium chloride is not available chlorine since it is not available for bleaching.

Calcium hypochlorite solution is generally prepared by mixing bleaching powder into a smooth paste with water and diluting further. The liquor is filtered through a sieve into a large concrete tank and diluted with water to roughly 10 times the weight of bleaching powder. The suspension is thoroughly mixed and allowed to settle. The clear supernatant liquor is transferred to another tank and diluted to the required strength before bleaching.

The mechanism of bleaching and the process are similar to sodium hypochlorite bleaching. The only difference is the formation of insoluble calcium carbonate (instead of soluble Na_2CO_3) when the calcium hydroxide is neutralised by carbon dioxide in air during the bleaching process.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
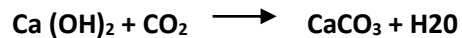
(Insoluble)

The presence of insoluble salts of lime in calcium hypochlorite bleaching imparts a harsh handle to the goods. This aspect makes it mandatory for the bleached fabric to be soured with dilute hydrochloric acid. Compared to bleaching with sodium hypochlorite, bleaching with bleaching powder solution gives less uniform results owing to inferior penetration. The bleachers, too prefer the use of sodium hypochlorite instead of bleaching powder, to overcome a number of difficulties faced with bleaching powder, including the problem of 'sludge' formed during dissolving the powder.

Since compounds that can liberate free chlorine are not environment friendly, use of both sodium hypochlorite and bleaching powder for bleaching of textiles has come under severe scrutiny.

Advantages of sodium/calcium hypochlorite

a) Low chemical cost.

b) Low energy input.

c) Low cost of equipment.

Disadvantages

a) The formation of a high level of AOX (absorbable organic halogens) results in environmental hazards.

b) Rapid bleaching process is not possible with hypochlorite.

c) There is a danger of yellowing of bleached fibre on storage (after yellowing).

d) There is also a danger of tendering of the material if pH and temperature are no controlled.

e) Cotton goods must be scoured before hypochlorite bleaching.

f) The process imparts a harsh feel to the bleached fabric, particularly when calcium hypochlorite is used
g) Low storage stability of chemick (hypochlorite bleach) liquor.

h) The process degrades most dyes and fluorescent brightening agents.

Souring

Souring is an acid treatment generally given to hypochlorite bleached goods. After bleaching and washing, 'souring' is necessary for the following reasons

i) It is very difficult to remove traces of alkali even after thorough washing. The alkali needs to be neutralised, otherwise it may get concentrated and result in the formation of oxycellulose during drying.

ii) In case of bleaching powder, the calcium carbonate formed during the bleaching is deposited on the fabric and cannot be removed by Simple washing. It imparts a harsh feel to the cloth.

Dilute hydrochloric acid at room temperature is generally used as the acid for souring. The goods may be impregnated with the acid in a rope washing machine ensuring uniform treatment. Alternatively, the goods may be soured in cisterns for about 30 minutes to one hour.

Sulphuric acid may also be used for souring when bleaching is carried out with sodium hypochlorite. But it is not suitable when bleaching with calcium hypochlorite because of the formation of calcium sulphate, which will be deposited on the fabric yielding a harsh feel. The reaction with hydrochloric acid on the other hand gives the soluble chloride. Complete removal of the acid is necessary after souring before the cloth is dried. Any traces of acid will cause degradation of the cellulose material because of increased concentration of the acid on drying.

It must also be ensured before souring that the goods do not contain hypochlorite which has been used in the bleaching process because over bleaching may take place during souring. Presence of hypochlorite in souring will cause intensive action of Hypochlorite by decreasing pH of the solution to the neutral level. To avoid this factor, the goods may be given an "antichlor" treatment with a solution of sodium bisulphite or sodium thiosulphate, which destroys the residual hypochlorite in the fabric.

Precautions during souring

I. Control of concentration of the acid solution.

II. Control of the process temperature.

III. Intermediate local drying of fabric should never be allowed.

IV. Optimum dwell period should be standardised.

Antichlor treatment

An antichlor treatment with a dilute solution of sodium bisulphite ($NaHSO_3$) or sodium thiosulphate ($Na_2S_2O_3$) or sodium hydrosulphite ($Na_2S_2O_4$) or any other inexpensive reducing agent may be given after the hypochlorite treatment to ensure removal of any residual chlorine from the bleached fabric. Hence the formation of chloramines (product of chlorine and residual amino acids present in the material), which cause after-yellowing of the material, is prevented.

In both the cases of souring and antichlor treatment, the cloth has to be thoroughly washed alter each process. Sometimes a "sweetening-of "is given by treating the fabric with a dilute solution of sodium carbonate or ammonium carbonate at room temperature as a precautionary measure to get rid of the problem of incomplete removal of the mineral acid used in souring.

Peroxide Bleaching

Hydrogen peroxide is a universal bleaching agent capable of application in bleaching with almost all textile material including wool, silk and man-made fibres. Since bleaching with hydrogen peroxide is carried out at raised temperatures it is possible to utilise this chemical in a one-stage process that combines both scouring and bleaching.

Hydrogen peroxide (H_2O_2) is a colourless liquid soluble in water. It is highly stable under acidic conditions but is unstable as alkalinity increases, as shown below

pH of Peroxide	Stability
1 to 3	High
4.5 to 5	Good
7.0	Medium
11.5 to 13	Lowest

The concentration of hydrogen peroxide is normally expressed in terms of volume i.e. volume of oxygen available per volume of hydrogen peroxide. For example,

20 volume hydrogen peroxide means 20 litres of oxygen are available from one litre of hydrogen peroxide on its decomposition.

Calculation of the active oxygen content of peroxide solutions of various strengths

The bimolecular reaction for the self-decomposition of hydrogen peroxide is:

$$2 H_2O_2 \longrightarrow 2H_2O + O_2$$
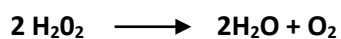
On the basis of molecular weights,

2x 34 g 100% produces 2 x 16 g active oxygen.

Active oxygen % = 16 x 100 / 34 = 47.05%

Thus: hydrogen peroxide (100%) contains 47.05% of active oxygen.

From this relationship, the percentage active oxygen (X) can be calculated for any peroxide solution by using the formula

X = 47.05 x C / 100

where C is the concentration (w/w%) of the hydrogen peroxide solution.

Example 1

How much active oxygen, in terms of per cent and grams, does hydrogen peroxide (35%) contain?

Active oxygen % = 47.05 x 35 / 100 = 16.46

Thus, expressed on weight basis,

1000 g of hydrogen peroxide (35%) contains 164.6 g active oxygen.

An approximate relationship between volume strength of hydrogen peroxide and per centage of hydrogen peroxide by weight is as follows:

Volume strength	Percentage of H_2O_2 (w/v)
100	30.00
130	39.00
160	48.00

Chemical reactions in peroxide bleaching

The oxidation potential of hydrogen peroxide is fairly low. It gives out oxygen very easily with the generation of heat as shown in the equations below.

1. $H_2O_2 \longrightarrow H_2O + (O) + x$ kcal   **Autolysis**

2. $H_2O_2 \longrightarrow H^+ + HO_2^-$ **Dissolved in aqueous medium**

3. $HO_2 \longrightarrow OH^- + (O)$ **Bleaching reaction**
   atomic oxygen
   (bleach active)

4. $NaHO_2 \longrightarrow Na^+ + HO_2^-$ **Bleaching reaction in**
   alkali medium (activation)

5. $2 H_2O_2 \longrightarrow 2H_2O + O_2$ **Decomposition**
   molecular oxygen
   (bleach inactive)

In aqueous medium hydrogen peroxide dissociates as shown in Equation 2 above. The HO_2^- (perhydroxyl ion) is highly unstable and in the presence of oxidisable Substances (impurities in cotton) it is decomposed as in Equation 3. On addition of caustic soda, the concentration of decomposable HO_2^- increases (sodium hydroxide activates hydrogen peroxide). In order to retard rapid decomposition of the unstable HO_2^- and formation of bleach active oxygen and at the same time prevent formation of bleach inactive molecular oxygen (Equation 5) the bleach bath has to be stabilised using a stabiliser.

Stabilisers in hydrogen peroxide bleaching

As hydrogen peroxide is made to release the perhydroxy! ion (HO_2^-) during the bleaching process through the addition of alkali, there is always the possibility of rapid decomposition of the peroxide. To ensure a fairly uniform availability of the perhydroxyl ion for the bleaching action, stabilizers are used.

Common stabilisers

The commonly used stabiliser is sodium metasilicate (Na_2SiO_3). It is highly effective and also low in cost. The use of slightly hard water is preferred for hydrogen peroxide bleaching as the presence of magnesium salts in water improves the effectiveness of sodium silicate stabiliser. For this reason, when soft water is used it may be necessary to add small amounts of magnesium sulphate ($MgSo_4$) and magnesium chloride ($MgCl_2$) to the bleach bath.

Non-silicate stabilisers

Although sodium silicate is both effective and economical the problems associated with silica deposits on the fabric and machinery have given rise to the development of alternate non-silicate or organic stabilisers. These products are blends of organic materials With or without magnesium salts and include the following.

1. Organic sequestering agents
2. Certain surfactants
3. Polymeric materials
4. Protein degradation products
5. A mixture of two or more of the above.

Advantages of peroxide bleaching

a) There is generally no need for thorough scouring before peroxide bleaching.

b) Hydroxide peroxide has excellent storage stability.

c) It is environmentally acceptable as it has no absorbable halogen.

d) Bleaching can be carried out under a variety of conditions (hot or cold). Single stage desizing, scouring and bleaching or only scouring and bleaching are possible.

e) Hydrogen peroxide is compatible with optical brightening agents.

f) It produces durable whiteness with good absorbency.

g) It involves low risk of chemical damage to cotton.

h) Peroxide bleaching requires a low quantity of water.

The disadvantages are its high cost, high risk of local damage to cotton and wastage of peroxide due to possible metallic contamination in water, and equipment and high energy (heat) inputs.

Bleaching with Sodium Chlorite

As a bleaching agent, sodium chlorite ($NaClO_2$) is versatile and may be used not only for cotton but also for many other fibres and mixtures with man-made fibres, but not for wool and silk. Sodium chlorite is more expensive than peroxide but has the advantage of very little tendering of material due to its relative insensitivity to traces of metal ions. Sodium chlorite is a fine white powder and when mixed with a small quantity of sodium carbonate it can be stored in the solid state indefinitely at room temperature.

Mechanism of chlorite bleaching

Sodium chlorite is soluble in water to give a stable solution with a pH of about 10. An acidified solution of sodium chlorite contains chlorous acid, the amount of which depends on the pH of the bath and its temperature. Chlorous acid ($HClO_2$) is unstable, decomposing to chlorine dioxide, chlorate, and chloride ions and to a small extent to oxygen under hot conditions depending upon change in pH from alkaline to the acidic according to the following three reactions.

i. $5ClO_2 + 2H^+ \longrightarrow 4ClO_2 + Cl^- + 2OH^-$

ii. $3ClO_2 \longrightarrow 2ClO_3 + Cl^-$

iii. $ClO_2 \longrightarrow 2Cl + 2(O)^-$

Reactions (i) and (ii) are relevant for bleaching, while Reaction (ii) leads to a loss in bleaching capacity due to the production of chlorate.

Acidified chlorite solutions are very reactive and cause corrosion to commonly used metallic vessels. Even among stainless steel, only that with high molybdenum content shows resistance. For this reason, vessels lined with resistant materials such as titanium, glass or ceramics are used. However, with careful control of pH of the bleach liquor and by addition of sodium nitrate (corrosion inhibitor) the corrosion problem is considerably reduced.

Bleaching process: The bleaching liquor may be made up with sodium chlorite (1-29) and a wetting agent and brought to a pH around 4.0 with addition of acetic or formic acid at 80 -85°C for 2-3 hours of

bleaching action. Chlorite bleaching carried out in open-with fabric consists of padding it with bleach liquor in a padding mangle at room temperature with 10 g/l of sodium chlorite at T00% expression. The cloth may be steamed or heated and passed into a J-box for a dwell period of 60 -90 minutes at 80 - 85°C. Alternatively the padded material may be rolled up and allowed to stand overnight; it is then washed as usual.

Advantages of chlorite bleaching

a) Pre-scouring or vigorous alkaline treatments of scouring are not necessary for chlorite bleaching and can even be avoided.

b) Chlorite bleaching effectively bleaches the lignin present in the woody matter.

c) Good whiteness is obtained without the necessity of kier boiling (thus saving in water consumption).

d) Soft fabric handle and good sewability is obtained due to non-removal of fats.

e) There is the least risk of chemical damage to cotton in chlorite bleaching.

f) The process is also the least sensitive to metallic contamination in the process Water

Disadvantages

a) There is the possibility of liberation of toxic chlorine dioxide gas.

b) The equipment is expensive because of the need for corrosion resistant material.

c) The chlorite-bleached fabric has poor absorbency and is therefore not suitable for further dyeing or printing.

d) Sodium chlorite is very expensive.

e) It is incompatible with optical bleaching agents.

Bleaching of Silk

Oxidative and/or reductive bleaching processes can be used for getting brilliant and bright shades in dyed silk. Bleaching generally follows degumming. As a rule, mulberry silk generally already reveals a light colour after degumming, and bleaching is consequently necessary only for a full white. On the other hand, bleaching is almost always necessary for obtaining brilliant shades with degummed tussah silk owing to its inherent colour that depends on tussah quality. For a full white, optical whitener can be added to the subsequent reducing bleach bath after oxidative pre-bleaching.

I. Silk is bleached for example in accordance with the following processes:

II. Oxidative bleaching with 35% hydrogen peroxide and sodium pyrophosphate ($Na_4P_2O_7$).

III.   Reductive bleaching with stabilised sodium dithionite (i.e. hydrosulphite).

IV.   Bleaching and brightening (full white): optical brightening is mainly effected after Oxidative pre-bleaching in the reduction bleaching bath.

Bleaching of Wool

There are four methods of wool bleaching.

1. Bleaching using reducing agents

2. Bleaching with hydrogen peroxide

3.Oxidative/reductive bleaching

4. Activated peroxide bleaching.

Bleaching using reducing agents

The bleaching action of the reducing agents used for bleaching wool is probably due to the action of bisulphite ions (HSO_3^-). In practice, there are basically two methods: either by exposing the wool to Sulphur dioxide gas (SO_2); or by treating the wool in a liquor containing reducing agents, such as sodium bi-sulphite ($NaHSO_3$), sodium dithionite ($Na_2S_2O_4$), sodium or zinc formaldehyde-sulphoxylate ($NaHSO_2CH_2O$) or $Zn(HSO_2CH_2O)_2$).

The use of reducing agents for bleaching wool is relatively limited. The principal Reasons for this are that use of Sulphur dioxide gas often results in an unlevel appearance and the whiteness achieved with reducing agents is not permanent (the original colour of the fibre tends to return on exposure to air, especially when the wool is exposed to strong sunlight). This latter effect is due to an oxidation process which reverses the original reducing action.

Bleaching wool with sodium bisulphite

In this method the goods are steeped in a solution of the following reagents for two hours.

Sodium bisulphite 2°Tw
Sulphric acid 1°Tw
The goods are then squeezed, washed and dried.

Sodium hydrosulphite

The above treatment may also be carried out with sodium hydrosulphite in which case steeping is done at 50°C for one hour to have a similar bleaching effect.

Bleaching wool with oxidising agents

Wool possesses a natural yellowish-brown colour, but some wools are brown and black. The fibre therefore needs a bleaching treatment for production of white goods and also for dyeing of bright pastel shades. Oxidising agents like hydrogen peroxide, potassium permanganate and sodium chlorite have been used in wool bleaching. Potassium permanganate and sodium chlorite give the bleached wool a slightly pinkish colour, so it requires an after treatment with sodium bisulphite or hydrosulphite. These two agents have therefore not gained much importance in the bleaching of wool. Hypochlorite does not have any bleaching action but causes a yellow discoloration and further the use of higher alkalinity as required in hypochlorite bleaching, is dangerous for wool fibre as it produces a serious tendering effect.

Bleaching wool with hydrogen peroxide

Hydrogen peroxide is the most widely used bleaching agent for wool. The whiteness produced is much more permanent than by any other method. Hydrogen peroxide bleaching in the case of cotton, may be carried out at elevated temperatures but in case of protein fibres i.e. wool and silk, controlled alkalinity and the temperature are two important factors. The degree of alkalinity required for activation of hydro- gen peroxide will be sufficient to damage the polypeptide chains if the temperature exceeds 60°C. The recommended range of pH for bleaching of wool therefore lies between 8 -8.5 with temperatures well below 60°C.

Catalysts

Traces of metals like iron and copper cause rapid decomposition of peroxide and further result in disintegration of the fibre i.e. tendering, which may not be revealed until the goods are in the hands of the consumer. Growth of mildew or micro-organisms particularly when wool is stored under alkaline conditions in warm atmosphere, takes place and results in rapid decomposition of hydrogen peroxide. When such a load is immersed in a bleach bath, the peroxide is decomposed within 20 -30 minutes.

Stabiliser

As in the case of bleaching cellulosic fibres, peroxide bleaching requires the use of stabilisers for controlled decomposition of the hydrogen peroxide. The widely used stabilisers in wool bleaching are sodium silicate, sodium pyrophosphate and Stabiliser C (a mixture of sodium oxalate and sodium pyrophosphate).

Effect of pH

The most suitable range of pH for wool bleaching is 8 to 8.5. If the pH is too high,

I.   Rapid decomposition of hydrogen peroxide takes place with evolution of oxygen before the perhydroxyl ion has an opportunity to exert bleaching action,

II.   Secondly, degradation of wool, accompanied by loss of strength and wearing power, takes place.

It is desirable that pH is continuously checked and adjusted during the bleaching process. Theoretically any alkali can be used. In practice sodium hydroxide and sodium carbonate are not used because delicate pH adjustments are not possible. Liquor ammonia finds use in bleaching of wool but it has no stablising property and tends to cause excessive loss of peroxide. Advantage of mild alkaline stabilisers (like sodium pyrophosphate, sodium silicate and tetra-sodium pyrophosphate) is taken in wool bleaching. The most commonly used is sodium silicate, which is free from any harmful action on wool fibres, it is however important that the goods arc thoroughly washed after bleaching, as traces of silicate if left, will result in a harsh fabric handle.

Method of bleaching:

Bleaching is carried out in a stainless steel or wooden vessel containing a 2-volume solution of hydrogen peroxide and 0.5% sodium silicate or Stabiliser Cat 50°C. The scoured material is entered and worked for 20 -30 minutes and then allowed to stay in a cooling bathfor3 -4 hours or overnight. After steeping. it is taken out, rinsed, soured with dilute acetic acid and rinsed again. Heavy fabrics like worsted and gaberdines may require a 6-volume solution of hydrogen peroxide. Sometimes it is desirable to avoid alkaline peroxide bleach for example when fabric contains stripe-effect dyed with acid dyes. Prolonged immersion in alkaline solutions under such circumstances will result in staining of the adjacent undyed regions. These dyes however are fast to acidic conditions. There is also less degradation of wool with an improved handle when peroxide bleach is done under acidic conditions.

When the above method is used, the amount of degradation is almost negligible. Stabliser KN (based on acid fluoride) has been specially developed for acid bleaching with peroxide. It is used in concentrations in the range 0.8%- 1%, which will be sufficient to stablise the pH between 3.9 to 4.0. The acid bleaching is more Suitable for blankets as it leaves the desired lofty handle and the bright coloured threads do not cause staining on adjacent portions.

This method may also be used for bleaching of wool/cotton unions. Besides hydrogen peroxide, sodium peroxide and sodium perborate are also used for bleaching. Depending on requirements, the material may also be treated with optical brighteners.

Bleaching of Polyester and its Blends

100% Polyester

The bleaching of 100% polyester is done only in exceptional cases where a perfectly white material is required. The best bleaching agent for this purpose is Sodium chlorite. The following recipe and bleaching conditions are used.

Recipe

Sodium chlorite - 2 to 5 g/l

Sodium nitrate - 1.5 to 2.5 g /l

85% Formic acid - 1 to 2.5 g/l (to get pH 4.5).

Temperature - Boil

Time 1 to 1 1/2 hours

The polyester fabric is treated as indicated above, ensuring that the pH is set at around 4.5. The bleached fabric is hot washed and finally given a cold rinse before drying This process is claimed to remove the slight yellowing caused by any previous heat treatment process.

PIC blends

In the case of P/C blends, it is invariably the cotton component that is bleached. Thus, the bleaching agents that are generally used for 100% cotton, like sodium hypochlorite, hydrogen peroxide or sodium chlorite, may be used, by means of batch, semi- continuous or continuous processes.

Bleaching of Synthetic Polyamide Fibres

Nylon fabric is scoured with a non-ionic detergent (1 -2 g/l) and trisodium phosphate (1 g/l) or soda ash (0.5 g/l) at 60°C for 30 minutes. f necessary, sodium hydrosulphite (0.5 -1 g/l) is added for the complete removal of the tint. The fabric is then thoroughly washed and dried before it is heat set at 180°C for 30 seconds or at a lower temperature of 140 -150°C if it is made of crimped yarn. Nylon fabric is rarely bleached. If at all this is required, a mild sodium chlorite (0.1 -1 g/l) plus acetic acid (for pH 4) bleaching treatment is given at 70°C.

Chemicals used for bleaching nylon

Sodium chlorite -1 g/l
Nitric acid - 2 to 3 to adjust the pH
Temperature - Boil
Time - 30 minutes

Bleaching of Acrylic Fibre and its Blends

Bleaching of acrylic fibre

Acrylic fibre is generally white in appearance and does not normally require to be bleached. The fibre material is scoured in liquor containing1.5-2 g/l of a non-ionic detergent at around 85°C for 45 to 60 minutes to remove the spin finish oil, identification tints and any adventitious dirt and dust.

If extra-white fibre is required the fibre has to be bleached. The hypochlorite bleaching agents like sodium hypochlorite are not used for acrylic fibre, as the highly alkaline conditions of bleaching would affect the fibre. Hydrogen peroxide bleaching is more suitable, but only if mild alkali in used and the pH is under control. The safest way to bleach acrylic fibre is with sodium chlorite. A typical recipe is given below.

Sodium chlorite -1.5 to 2.5 g/l
Sodium nitrate -2.5 to 5 g/l
Formic or oxalic acid to obtain a bath pH of 4.
The goods are treated in the above liquor at 85°C for 30 45 minutes and then washed. The washed material is then given an antichlor treatment in a 10 g/l solution of sodium bisulphite to remove traces of chlorine from the fibre. Finally, the goods are washed thoroughly.

Bleaching of acrylic/cotton blends

This blend assumes great importance in recent times on account of the attractive features of both of these fibres. Acrylic fibre confers the properties of extensibility elasticity, toughness, and good abrasion and wear resistance, while cotton contributes to the comfort aspects and the cool, pleasing handle of the blend. Further, in times when the cotton economy is not at its best, the blend affords an excellent substitute

Acrylic fibre cannot withstand high alkalinity. If only the cotton component is to be bleached, a hydrogen peroxide bath in which the pH is under good control is the best. The blended material is treated in a peroxide bath, containing 7 g/l of 35% hydrogen peroxide and 4 g/l of sodium silicate, at 90°C for 60 minutes. The bleached material is then washed thoroughly. If both the fibres need to be bleached, the best bleaching agent is sodium chlorite. A typical recipe is given below.

Recipe

80% Sodium chlorite - 1.5 to 2.0 g/l
Formic acid - 1.5 to 2.0 g/l
Sodium pyrophosphate - 0.5to 1.0g/l
Detergent - 1.0 g/l

The blended material is treated in liquor of the above composition for 1 to 1 1/2 hours at 85^0 C . After the treatment, the goods are washed, given an antichlor treatment with a 10 g/l solution of sodium bisulphite at 60°C for 30 minutes, to remove traces of chlorine, and finally washed.

Bleaching of acrylic/wool blends

Acrylic/wool blends offer the advantages of both the fibres. The acrylic fibre is a comparatively strong fibre and has good abrasion resistance and wear properties. Wool provides comfort characteristics, because of its high moisture regain, and softness of handle to the blend.

The acrylic/wool blend is first scoured in a bath containing 1.5 -2 g/l of a non-ionic detergent at 75 -80°C for 1% to 2 hours to remove the spin finish oil, dirt, etc., from the acrylic component, and then washed. Next, the wool component is carbonised by impregnating the blend with a dilute solution of sulphuric acid, then drying (at 85°C) and finally baking (al 110°C).

The material is then bleached with liquor containing 3 - 5 g/l of 35% hydrogen peroxide (115-volume solution) and 2.5 g/l sodium silicate at 55°C for 60 minutes to bleach the wool component. If the acrylic component acquires a yellowish tint due to this treatment, it can be removed by means of a run in a bath that includes a detergent and formic acid.
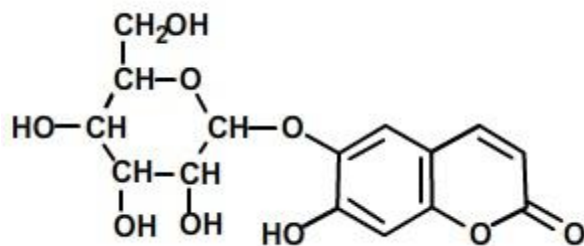
Optical Brightening agents

Most of the textile materials, especially the natural ones, appear slightly yellowish of off white even after they have been bleached. They are not bright white. The reason lies in slight absorbance by these substrates in blue region of visible light which leaves these materials appearing as slightly yellowish. This can be seen in the following figure.
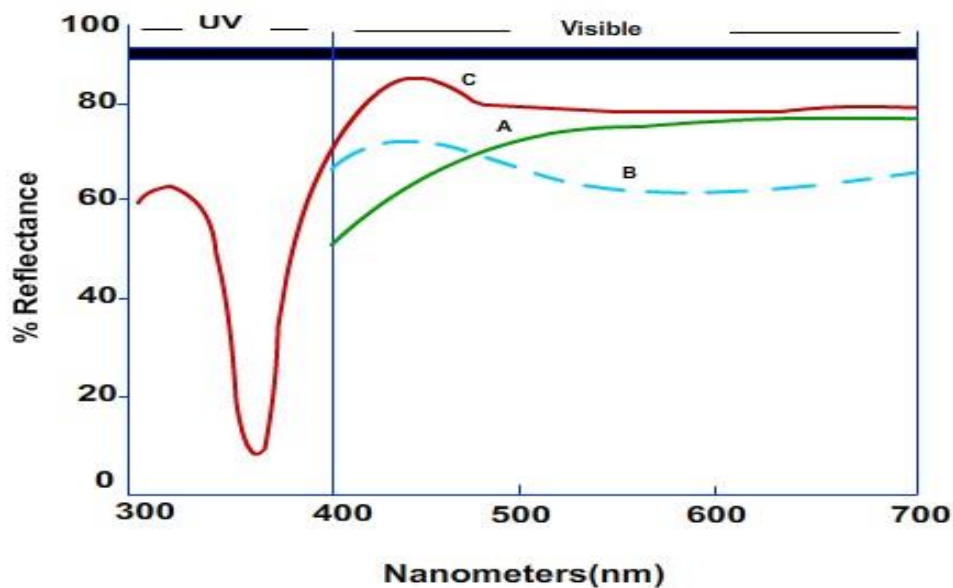
Across cultures, bright white has been regarded as signifying purity and hence there have been efforts to achieve brighter whites. Attempts have been made to tint white goods with blue pigments since bluish whites are preferred over whites with yellowish or greenish tinge.

To make whites brighter, one needs to increase the reflectance of the bleached goods further. This is possible with certain additives which absorb UV component of solar radiation and emit in visible range (preferably in blue violet region). Thus, the overall reflectance of the goods becomes higher than that of bleached goods with a blue tinge to it, making it appear much brighter.

The first recorded evidence of OBA application happened in 1929 when Paul Krais applied aqueous extract of aesculetin-6-glucoside (a naturally occurring OBA) on line

Aesculetin-6-glucoside

These agents have been known as Fluorescent Brightening Agents (FBA) or Optical Whiteners (OBA). They are distinct from blueing agents in that while blueing agents suppress overall reflectance, the OBAs actually enhance it.

Mechanism of OBA action-

OBAs are designed to absorb light between 340 to 380 nm (UV spectrum) & emit it in the range 425 to 450 nm (visible spectrum).

Effective OBAs must absorb strongly in UV region and emit a large part of the absorb energy in the visible region. OBA molecules have an extended conjugated bond system as it is capable of strong fluoresce.

In the figure given below, the ground and excited energy levels. (S1, S2……) are shown. So S1, S2…… represent singlet states with paired spins & T1, T2……represents triplet states with unpaired spins.

The energy levels are further subdivided in to vibrational levels.

When an OBA is exposed to electromagnetic radiation, the electrons are transported to one of the excited energy levels from the ground level. The energy state and the vibrational level to which it is transported depends on the amount of energy absorbed (E=hv) within an energy level
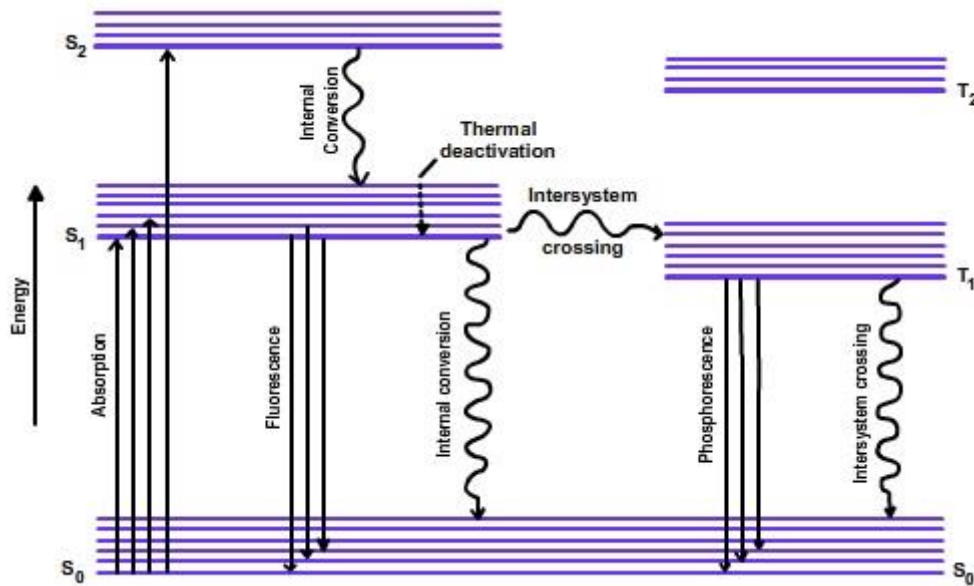
Absorption and fluorescence processes

(S1, S2……). The electrons lose the energy very quickly (10-12s) to come down to the lowest vibrational level in existing energy level. The return of the electron from the lowest vibrational level of an excited energy state to one of the vibrational levels in the ground state (S_0) is known as the fluorescence, and is accompanied by release of energy in the form of EM radiation (emission) corresponding to the frequency given by the relation

$E = h\nu$

Since the energy released by the electron during fluorescence is always lower than the energy absorbed, the wavelength of emitted radiation is always higher than that of absorbed radiation.

Hence, if absorption occurs in UV region, the emission may occur in violet or blue region of visible spectrum. The difference between the wave number of absorption and emission is known as stokes shift. For maximum effectiveness, an OBA should absorb around 370 nm and emit around 430 nm for a Stokes's shift of around 60 nm. Depending on the nature of OBA, it can produce violet, blue or green hued whiteness. This depends on the wavelength/wave number in which the OBA is emitting. However, the hue of the OBA can also change with the concentration level. With increasing concentration, the whiteness produced by an OBA increases initially. However, at higher concentration it starts aggregating & a shift in fluorescence may be observed. A blue tinged fluorescence may turn in to greenish hue which is undesirable & rather than appearing white, the material may appear coloured. This is shown in figure below.
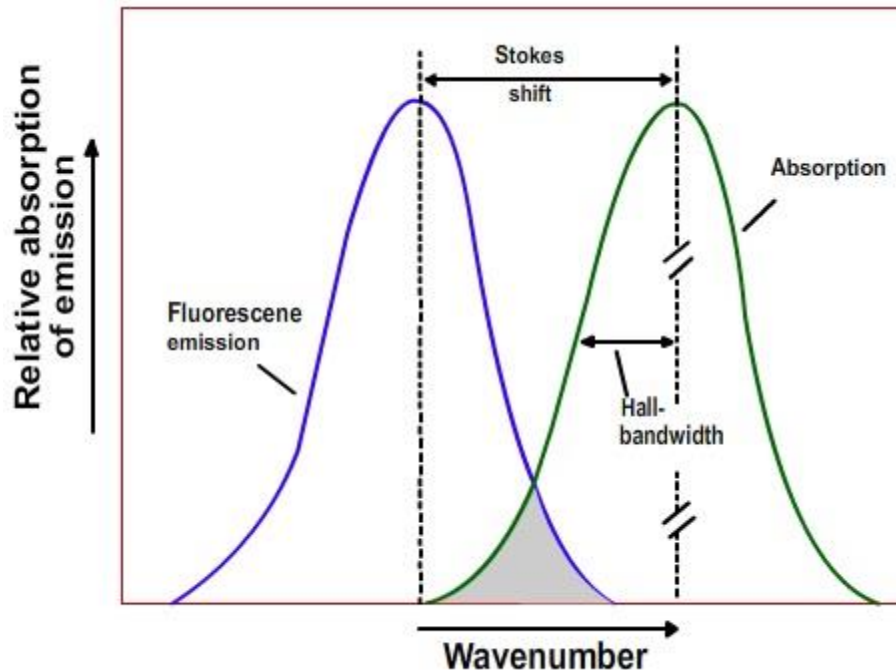
Typical absorption and emission curves for an FBA

Chemistry of FBAs

Just like dyes, different OBAs are suitable for different fibre types. Therefore, OBAs for cotton, wool & silk are anionic in nature, for PET hydrophobic and for acrylic, cationic.

In general, OBAs for cotton have poor light fastness (1-3) meaning they need to be applied over and over again to maintain the whiteness. For the same reason white paper turns yellowish gradually due to destruction of OBA in it.

OBAs for cellulosic substrates

Brighters for cotton are anionic in nature and are applied in a way similar to the application of direct dyes. A range of products varying in substantivity from high to low is available. Low substantivity OBAs are suitable for application by continuous method while the high substantivity ones are applied by exhaust method. OBAs can be applied during bleaching or in a separate step after bleaching.

Since fading of OBAs on cellulosic substrates is faster due to poor light fastness, they need to be fortified frequently. This is generally done by formulating them in washing soaps and detergents.

The most common OBAs for cellulosic fibres are based on triazine derivatives of diamino stilbene disulphonic acid (DAST) with following chemical structure.
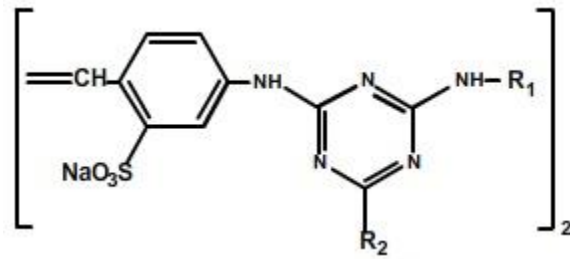
Where M is alkali metal like Na or K, or ammonium cation

R1 is an aromatic amine residue/ its derivative
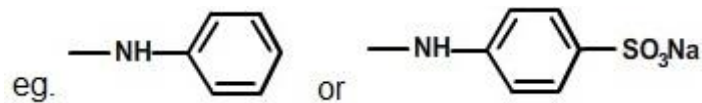
R2 is generally aliphatic amine derivatives

e.g. N(CH2CH2OH)2 or -NH-CH2CH2OH

The following product (vic triazol)
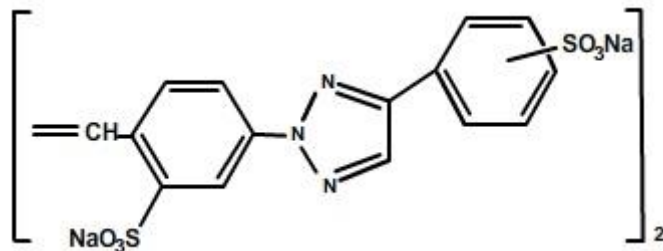
Has a light fastness of 5 on cotton, which is very high for OBAs on cotton. It is stable to chlorite & hypochlorite bleaching and can be applied along with resin finish.

However, it is expensive.

Nylon –

OBA generally used for Nylon are anionic in nature like acid dyes. These are generally applied from an acidic bath pH – (4-5).
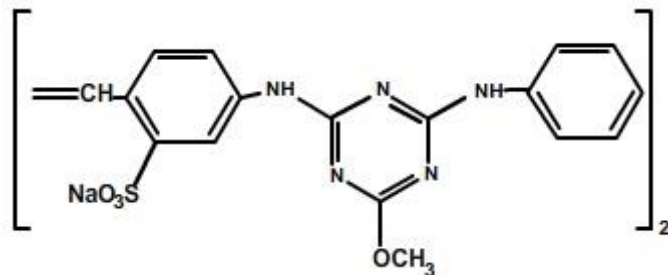
The vic- triazole is shown above.

Polyester-

The OBAs for polyester are disperse type. They can be applied by exhaust & pad-thermosol (continuous process) or by addition directly in the melt (mass brightening) like in mass coloration. Following OBAs are useful for polyester.

These can be applied by exhaust at 125-130 °C and by thermosol operation at 160-220 °C.
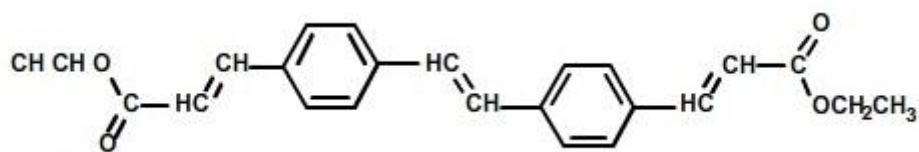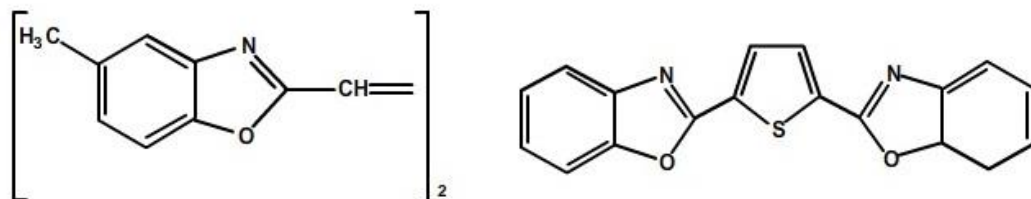
Can be applied by thermosol process above 190 °C. The light fastness of OBAs on PET is generally higher at 5-6.

Acrylic fibre -

OBAS for acrylic fibres are generally applied from acidic baths by exhaustion around boil.

Derivative of 1,3-diphenylpyrozoline (figure below) can produce very high whiteness of violet tinge, the OBA is unstable to chlorite bleach and can produce LF of 4.

$$Cl-C_6H_4-C(=N-N)-\text{pyrazoline}-N-C_6H_4-SO_2CH_2CH_2CONHCH_2CH_2N(CH_3)_2$$
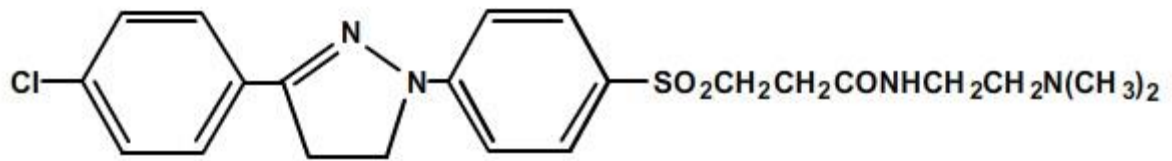
The following product is stable to chlorite and can be applied during bleaching itself. It can also give a light fastness of around 4.
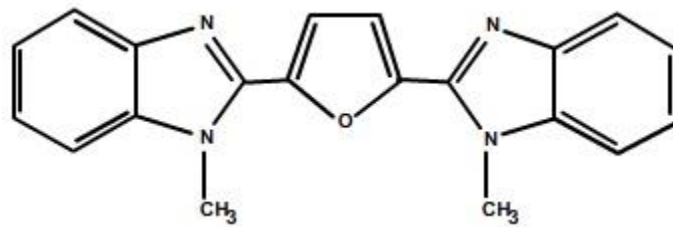
UNIT- V

DYEING & WET PROCESSING M/C

5.0 Introduction

5.1 Classification of dyes and pigments used in textile industry

There are basically two ways of classifying various dyestuffs:

1. According to use, and
2. According to chemical constitution.

The use-wise classification of dyestuffs is more important from a practical point of view and is given in **Figure.** The term 'synthetic dyes' is used for all dyes that are available in coloured form as 'readymade dyes'. Natural dyes are also included in the above classification as the extracts of a vast number of plants and some from animal origin are used for dyeing silk, wool and cotton.

Some vat dyes, azoic pigments and other pigments are available in insoluble form to the textile chemist. These are used without converting them into their soluble forms, generally for textile printing. Hence such colourants are classified under pigments, which are regarded as insoluble, just as dyes are regarded as soluble. The inclusion of optical brightening agents may be specially noted as these are regarded as colourless dyes having a fluorescent system instead of a typical chromophore system of a dye.
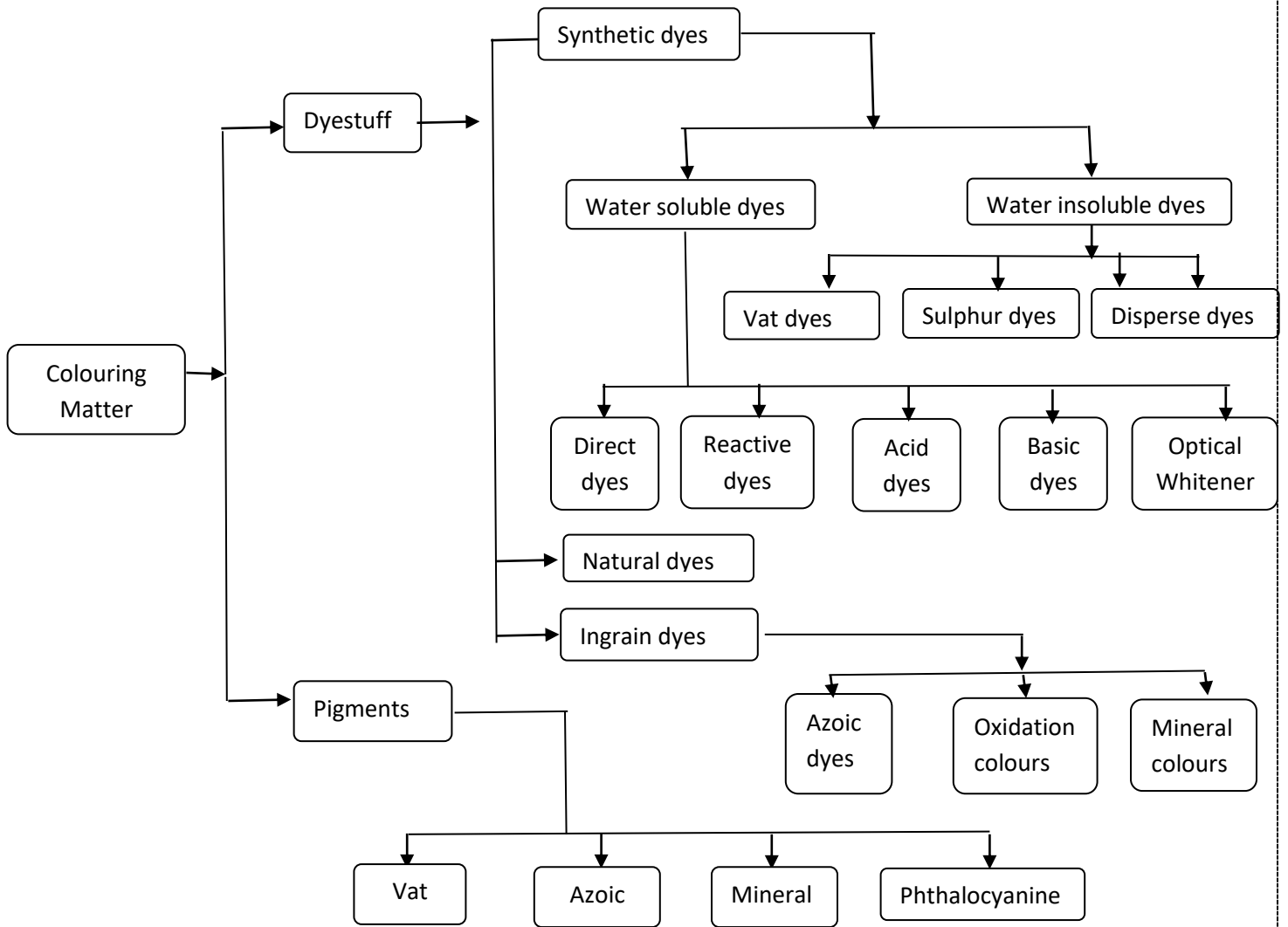
Figure. Classification of dyes and pigments

5.2 Comparison between natural and synthetic dyes.

Sl. No.	Natural Dyes	Synthetic dyes
1.	These are obtained from natural sources.	These are chemically synthesized.
2.	Natural dyes are ecofriendly.	Synthetic dyes are toxic in nature.
3.	Availability of natural dyes are limited.	Synthetic dyes are abundantly available.
4.	Poor colour yield.	Excellent colour yield.
5.	Reproducibility of shades are limited.	Easy reproducibility of shades.
6.	Natural dyes are limited in number.	Wide range of dyes are available for synthetic dyes.
7.	Natural dyes are biodegradable.	Synthetic dyes are non-biodegradable.
8.	Natural dyes are non-hazardous.	Synthetic dyes are hazardous in nature.
9.	Natural dyes are scarce and costly.	Synthetic dyes are readily available at low cost.
10.	Natural dyes give dull and muddy colour.	Synthetic dyes give a better glow and a range of colours.
11.	Range of shades are limited.	Wide range of shades.
12.	Natural dyes does not have direct affinity for the fibre.	Synthetic dyes possess direct affinity for the fibre.
13.	Natural dyes have poor fastness properties.	Synthetic dyes have moderate to good fastness properties.

5.3 General properties of dyes (solubility, affinity toward, Properties)

Substantivity/Affinity

The substantivity of a dye for a fibre can be defined as an **attraction between the fibre and the dye** under given dyeing conditions, whereby the dye is selectively extracted from an application medium by the fibre. For quantitative work the term affinity is used as it is more clearly defined and can be given a numerical value (usually in joules per mole). It is defined as the difference between the chemical potential of the dye in its standard state in the fibre and the corresponding potential in the dye bath.

In simple terms substantivity or affinity indicates the **ability of a dye to go from the solution phase to the fibre.**

Exhaustion

This is a measure of the proportion of the dye absorbed by the fibre in relation to that remaining in the dye bath. Thus, it indicates the **amount of dye that has moved from the solution into the fibre** under given dyeing conditions. It is also a measure of the substantivity of the dye for the fibre.

Exhaustion is expressed in terms of percentage. For example, if the exhaustion of a dye bath is 75%, it means that 75% of the dye in the dye bath has moved from the dye solution or dye liquor into the fibre.

The term exhaustion is mainly applicable to batch-wise dyeing which is also called "exhaust dyeing". Textile yarn and fabric are often dyed by the exhaust dyeing technique.

Material to Liquor Ratio

This expression refers to the weight: volume relationship between the fibre to be dyed and the total volume of dye bath. It is normally abbreviated as MLR and sometimes written as M:L ratio. An M:L ratio of 1:10 means that a dye bath volume of 10 litres is required to dye 1 kg of dry fibre.

The material to liquor ratio is also sometimes referred to as an inverse ratio and called the "liquor to goods ratio" or simply the "liquor ratio" and this ratio is given by the following expression.

Liquor to goods ratio = Total volume of dye liquor used in ml / Dry weight of material dyed in grams

Thus 5 g of material dyed at a liquor to goods ratio of 5:1 would use 5 x 5 = 25 ml dye liquor.

Alternatively, 3 g of material dyed in a dye bath of 60 ml has a liquor/goods ratio of 60/3 or 20/1 or 20:1.

Typical liquor ratios used in different types of machines

i) In all the liquor circulating machines like kier, jet dyeing and cheese dyeing machines the M:L ratio is 1:4 or 1:5.

ii) In a jigger it is 1:4.

iii) In a padding machine it is 1:1.

iv) In a winch it is in the range 1:10 to 1:25.

v) In an open beck the ratio would be 1:20 to 1:40.

The higher the M:L ratio, the larger is the volume of dye liquor, so lower is the concentration of dye, as dyes are always taken in terms of a percentage of the weight of the textile to be dyed. The lower the concentration of dye solution, the longer it will take to obtain a given level of dye absorption or shade.

Expression

The term 'expression' indicates the percentage increase in the weight of dry fabric after padding. For example, let us assume that the dry weight of a length of fabric is 1 kg. Let this fabric be saturated with dye liquor and 'padded' between the rolls of a padding mangle to squeeze out the excess liquor. If the weight of the wet fabric coming out of the padding mangle is 1.8 kg, it means that there is an increase in weight of fabric by 0.8 kg. The weight of dye solution in the padded fabric is 80% of the dry weight of the fabric. The 'expression' in this case is said to be 80%.

The higher the expression in a fabric being padded, the lower is the squeezing pressure in the padding mangle and vice versa. A fabric padded to an expression of 110% will contain more dye liquor than one padded to 90% expression, and so on. The former fabric has greater 'pick-up' than the latter case.

A useful formula for padding is,

Grams of dye liquor in 100 ml of pad liquor = Percentage of dye needed on fabric / Percentage of pick-up X 100

Shade Percentage

'Shade percentage' refers the quantity of dye taken for a dyeing expressed as a percentage of the dry weight of the fibre to be dyed. For example, if 1 g of a dye is taken for dyeing 100 g of a textile material, the shade percentage is referred to as 1% shade. And with reference to the dyed material, it is said to be dyed to a 1% shade. Similarly, if a kilogram of fibre is required to be dyed to a 3.5% shade, the amount of dye to be taken would be (1000 × 3.5)/100 = 35 grams.

Percentage depth of shade can thus be defined as parts by weight of dyestuff to be added to a dye bath per 100 parts by weight of material. Thus a 2% depth of shade would require the addition of,

2 g of dye in order to dye 100 g of material
or 1 g of dye in order to dye 50 g of material
or 0.1 g of dye in order to dye 5 g of material

When the weight of the dye to be added is small, it is common to prepare a concentrated solution of the dye and add a part of it to the dye bath. In such cases, the volume of stock solution to be added is often calculated from the formula,

ml of dye solution required or added = % of depth of shade x Weight of fibre to be dyed in g
Concentration of stock dye solution in g/100 ml

For example, if a 3% shade is required to be dyed on 4 grams of cotton yarn using a solution of one gram of dye in 200 ml of water (i.e., 0.5 g in 100 ml water), the ml of the stock dye solution required would be,

ml of dye solution required or added = 3 x 4/0.5 = 24 ml

5.4 Principles of dyeing.

The process of dyeing may be divided into three phases

i) **Adsorption** of the dyestuff at the fibre surface,

ii) **Diffusion** of the dyestuff through the internal structure of the fibre, and

iii) **Fixation** or 'anchoring' of the dye molecule at a suitable location or dye site.

i. Adsorption: In the first phase or step, the dye molecules in the dye bath move towards the fibre and those that are nearest to the fibre get 'adsorbed' on to the fibre surface. They form a very thin layer of molecules on the fibre surface. Other dye molecules still in the dye bath can be adsorbed only if this adsorbed layer moves further into the fibre. A schematic representation of a fibre showing the 'adsorption' of dye molecules on the surface of the fibre is shown in **Figure.**

Adsorption of dye molecules on the surface of a fibre
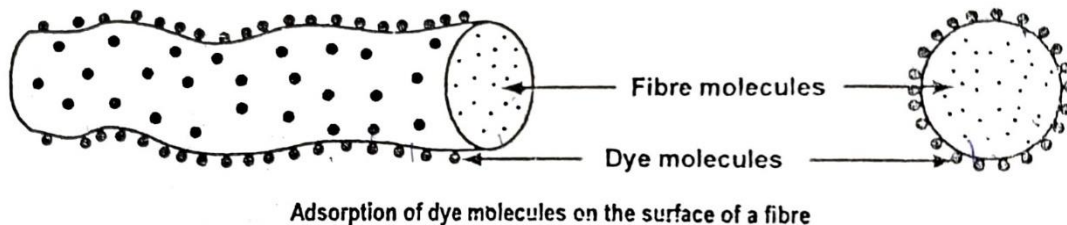
Figure. Adsorption of dye molecules on the surface of a fibre

ii. Penetration: In the second step, the adsorbed dye molecules enter the fibre structure and gradually penetrate or 'diffuse' into the pores or canals in the structure. The rate of penetration and the depth to which they get will depend upon the molecular characteristics of the dye, the molecular arrangement in the fibre and the dyeing conditions. Diffusion or penetration of dye in the fibre accounts for almost the whole of the dyeing time. The greater the penetration of dye into the fibre the brighter and better is the dyeing. Good penetration is thus the key to quality dyeing. Poor penetration results in dull, surficial dyeing with unsatisfactory colour fastness properties. Figure 2.7 shows schematic representations of dyed fibre, one with good dye penetration and the other with poor penetration.

Cross-section of a fibre with poor dye penetration called "ring dyeing"

This cross-section of a fibre with good penetration will appear brighter and show good fastness properties in comparison to the fibre on the left

Dye peneration in a fibre

Figure. Dye penetration in a fibre

iii. Fixation: The final step is one where the dye molecules find suitable locations or dye sites, where they get 'fixed' or 'anchored'. The forces by which the dye molecules are held thus inside the fibre vary in nature and strength and depend upon the dye-fibre relationship.

The exact nature of the forces holding dye particles to fibre surface is not fully understood, but the possibilities may be classified as follows:

Van der Waals' forces: Very weak forces of attraction are always present between the electrons of one atom and the nucleus of another in close enough proximity. individually these are very weak forces, but collectively they are considered to be of sufficient strength to be the most important attractive forces between dye and fibre. These forces of attraction are known as van der Waals' forces. Disperse dyes are held in a polyester fibre by means of van der Waals' forces.

Hydrogen bonds: These forces of attraction are weak forces set up between certain atoms in the dyestuff molecule when they are close enough to other atoms in the fibre. One of these atoms is the hydrogen atom, hence the term 'hydrogen bond'. Some direct and vat dyes are 'hydrogen bonded' in cellulose fibres.
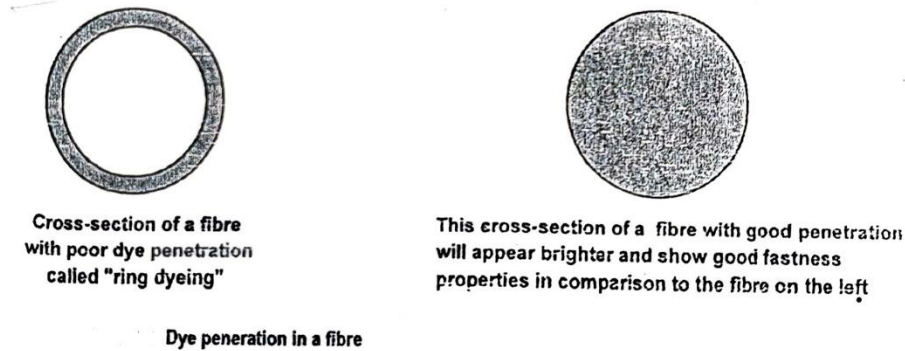
Salt linkages: In aqueous solution, dyestuff molecules split up into positively and negatively charged particles called "ions", one of which is coloured. Depending upon the particular class of dyestuff being considered, the coloured ion may be *cationic (carrying a positive charge), or 'anionic' (where the charge is negative). When strong electrostatic forces of attraction develop between the ions in a fibre and oppositely charged dyestuff ions, salt linkages or ionic bonds are said to be formed For example, when the (anionic) -SO, groups in an acid dyestuff gets close enough to attract a (cationic) -NH, group in wool, silk or nylon, the resulting bond is a salt linkage or an ionic bond or an electrostatic bond.

Covalent bonds: Bonds resulting in very strong chemical forces that are not easy to break except under severe conditions are called covalent bonds. The classic example is that of the combination of cellulosic fibres with reactive dyestuffs, where the hydroxyl group in the cellulose is covalently bonded to a suitable atom in the reactive dye.

The various types of bonds occurring for different dye-fibre combinations are illustrated in Figure.
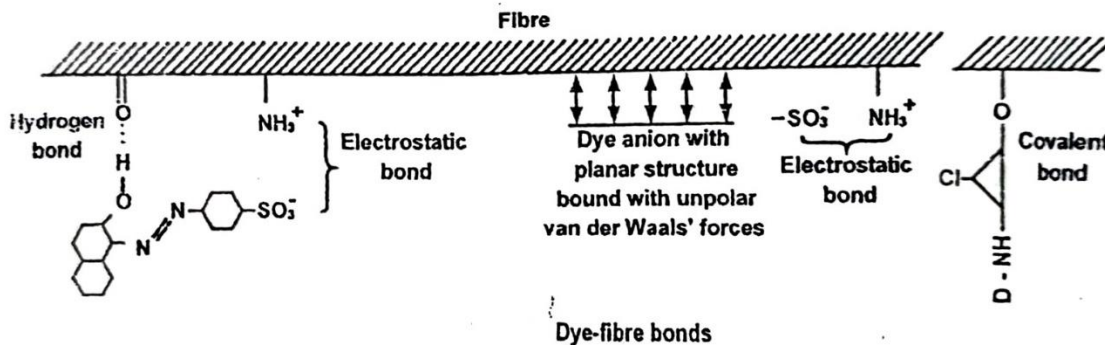
A comparison of the relative strengths of the bonds described above is indicated in Table 1 and the types of bonds predominately found in various dye-fibre combinations are listed in Table 2

Table 1 Comparison of the relative strengths of dye-fibre bonds

Bond type	Relative Strength
Van der Waals' forces	1.0
Hydrogen bond	3.0
Salt linkage (ionic bond)	7.0
Covalent bond	30.0

Table 2 Fibres, dyes and dye-fibre bonds

Fibre	Dye class having affinity	Type of dye-fibre bond
Cellulosic: Cotton, jute, rayon etc.	Direct, vat, solubilised vat and Sulphur	Van der Walls forces and hydrogen bonding
	Reactive	Covalent bonds
Protein/Polyamide: Wool, Silk, nylons	Direct, acid, metal complex and basic	Ionic or electrostatic bond
	Reactive	Covalent bonds
Polyester	Disperse	Van der Walls forces and hydrogen bonding
Cationic dyeable polyester	Cationic	Ionic or electrostatic bond

	Disperse	Van der Walls forces and hydrogen bonding
Acrylic	Cationic	Ionic or electrostatic bond
	Disperse	Van der Walls forces and hydrogen bonding

5.5 Dyeing of textiles of natural fibres [(Cotton by direct, reactive, vat, azoic& sulphur), (Silk and Wool by acid dye).

5.51 Dyeing of cotton with Direct dye.

Introduction

Direct dyes are also called **substantive dyes** because of their excellent substantivity for cellulosic textile materials like cotton and viscose rayon. This class of dyes derives its name from its property of having **'direct' affinity for cellulosic fibres** when applied from an aqueous solution.

Chemically, direct dyes are sodium salts of aromatic sulphonic acids and most of them contain an "azo" group as the main chromophore. Various manufacturers market direct dyes under different trade names. Some examples are given below.

Manufacturer	**Trade name**
Indokem	Incomine
Hindustan Ciba Geigy	Chlorantine, Solophenyl
Clariant	Solar
Atul Products	Atul Direct
ICI	Chlorazol

The structure of a direct dye is shown below. Note the -N=N- (azo) and the $-SO_3Na$ groups.
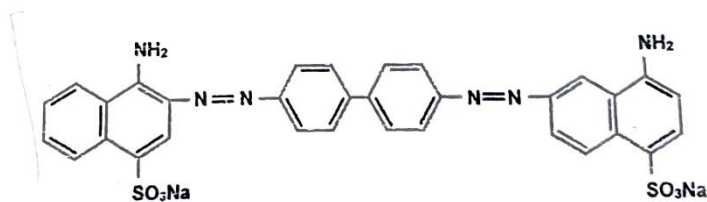
Properties of Direct Dyes

1. Direct dyes are soluble in water and have affinity for cellulose and protein fibres, especially wool.
2. Chemically the dyes are represented as sodium salts of sulphonic acid (DSO_3Na).
3. When the dyes are dissolved in water, the dye molecules get dissociated into ions (DSO_3^- and Na^+). During dyeing, the textile material absorbs the coloured anions from the dye solution. This is followed by the diffusion of the molecules into the fibre where they are finally retained or 'anchored' by means of physical forces.

$$D\text{-}SO_3H \xrightarrow[\text{Na}_2\text{CO}_3]{\text{Alkali}} D\text{-}SO_3Na \xrightarrow{\text{Water}} DSO_3^- + Na^+$$

| Dye with sulphonic Acid group | Sodium salt of sulphonic acid i.e., dye | Dye anion | Sodium cation |
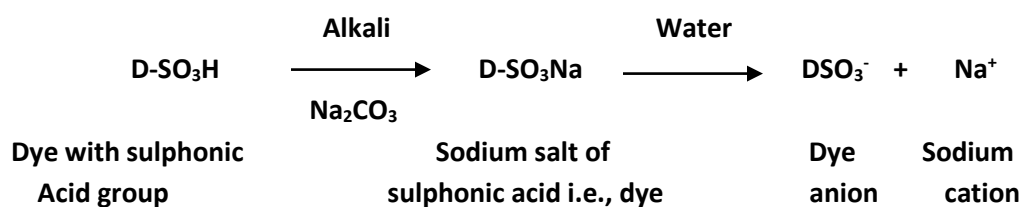
4. Owing to their water solubility, the dyes possess poor wash fastness. Light fastness, however, is poor to moderate, even good in some cases.
5. The fastness properties of these dyes can be improved slightly by means of certain after treatments.

Classification of Direct Dyes

The direct cotton dyes are classified into the following groups depending on the effect of electrolyte and temperature.

Class A: Self-leveling dyes

While using these dyes, the dyeing may be uneven in the initial stages but they get levelled on prolonged dyeing because of better migration properties. These dyes do not require salt for their exhaustion.

Class B: Salt-controllable dyes

These dyes do not migrate well and require salt addition for increased exhaustion. If uneven dyeing takes place initially, it is very difficult to correct the dyeing.

Class C: Temperature-controllable dyes

Similar to the Class B dyes, the leveling properties of these dyes are poor. They are also sensitive to salt and their exhaustion cannot be controlled with salt alone. These dyes require their exhaustion to be controlled by controlled rise of dye bath temperature.

When more than one dyestuff is required to match a given shade, dyes belonging to the same class should be preferred.

Mechanism of Dyeing

When cotton is immersed in a solution of a direct dye, the following mechanism takes place.

1. Fibre swelling in the liquor
2. Adsorption of the dye at the fibre surface
3. Diffusion of dye molecules into the interior of the fibre.

The phenomenon of adsorption and diffusion can be illustrated by microscopic views at different stages of dyeing of cotton as shown in **Figure.**

Undyed cotton   Cotton dyed at 100°C (few minutes)   Cotton dyed at 100°C (1 Day)

Diffusion of dye into fibre with time
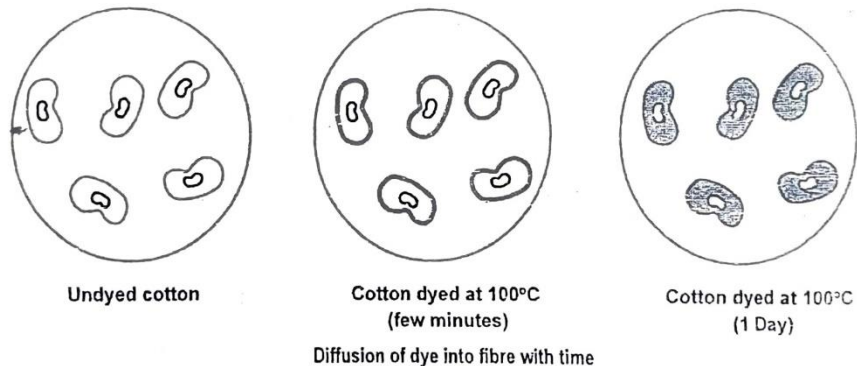
Application Procedures

The dyeing process basically involves two steps:

i) Preparation of the dye bath
ii) Dyeing.

Preparation of the dye bath

The dye is dissolved by pasting it with a small amount of water and soda ash (if required). Boiling water should then be added to the paste with constant stirring. If pasting is not done prior to the addition of boiling water, the dye may form into lumps, and this in turn will result in speckled dyeing. Stock solutions (i.e., concentrated solutions) are usually prepared and the required volume of these solutions is taken for dyeing.

Direct Dyes on Cotton

The dye bath is set with the required volume of the stock solution of dye, 0.5 to 1% soda ash and water to make up the desired M: L. ratio. The well-prepared material (desized, scoured and bleached) is entered in the dye bath at 40°C and dyeing is carried out for 15-20 minutes. The prescribed quantity of common salt is added in an even number of installments at intervals of 10-15 minutes. Common salt is generally preferred to Glauber's salt for reasons of economy. (Glauber's salt being anhydrous requires the use of larger quantities). The quantities of salt used are dependent on the shade being dyed and varies between 5 - 20% on the weight of material for light to heavy shades.

The temperature of dye bath is slowly raised to the boil (or the recommended maximum dyeing temperature). The dyeing is continued at this temperature, for a period of 45 - 60 minutes. The material is then allowed to remain in a cooling /bath for 15-20 minutes for obtaining better exhaustions. Finally, the goods are removed from the dye solution, squeezed/hydro extracted and dried. An after-treatment in a solution of a dye-fixing agent often precedes the drying step.

Typical recipe for Class A (self-leveling) type of dye

Direct dyestuff -	X% (owf)
Soda ash -	0.5 to 1% (owf)
Common salt -	5% (owf) for light shades
	10% (owf) for medium shades
	20% (owf) for dark shades
Temperature -	Boil
Time -	45 to 60 minutes

After-treatment of Direct Dyed Goods

The reasons for the popularity of direct dyes in the dyeing of cellulosic fibres are the low cost of dyeing and the simple dyeing procedure. As a matter of fact, these dyes do not possess adequate washing fastness properties and most of them fade in light. The use of direct dyes therefore becomes undesirable for material that will subsequently be washed frequently or continuously exposed to light.

A number of methods has been devised to improve the fastness properties of direct dyes. These after-treatments are based on principles like increasing the molecular weight of the dye and thus decreasing their solubility in water after dyeing. All the direct dyes, however, are not capable of such after-

treatment since, in many cases the colour of the final product changes i.e. it tends to become duller and sometimes the hue too is altered.

Some after-treatments that have been in use are summarised below:

1. Treatment with metallic salts

(a) Treatment with copper salts

Certain dyestuffs are capable of reacting with copper and showing remarkable improvement in light fastness properties. The dyed material is treated in a bath containing:

Copper sulphate (owf)	**0.5-2% on weight of the fibre (owf)**
Acetic acid (30%) (owf)	**0.5-2% (owf)**

The actual concentrations of the chemicals used depend on the depth of shade of the dyeing. The treatment is carried out at 80°C for 30 - 45 minutes. The material is then rinsed and dried. Commercial products such as Cuperantine, Cuprofix, Cuprophenyl, etc. have also been used instead of the above chemicals.

(b) Treatment with chromium compounds

Chromium atoms can be introduced in the molecular structure of certain direct dyes, resulting in more complex structures than those with copper compounds and hence provides a way of improving the washing fastness properties of the dyes. This treatment however does not alter their light fastness properties.

The dyed goods are treated in a bath containing:

Potassium dichromate	**2-3% (owf)**
Acetic acid (30%)	**2-5% (owf)**

The treatment is for 30 minutes at the boil. The goods are then rinsed and dried.

A combination of the treatments with copper and chromium compounds can be employed to get improvements in washing as well as light fastness properties. The dyed goods are worked in a bath containing the following:

Potassium dichromate	**0.5-2% (owf)**
Copper sulphate	**0.5 -2% (owf)**
Acetic acid (30%)	**1-5% (owf)**

The treatment is for 30 minutes at 80°C followed by rinsing and drying.

2. Treatment with formaldehyde

Increasing the relative size of the dye molecules of some direct dyes can also be achieved by treatment with formaldehyde, thereby yielding improved washing fastness properties. The dyed goods are treated in a bath containing:
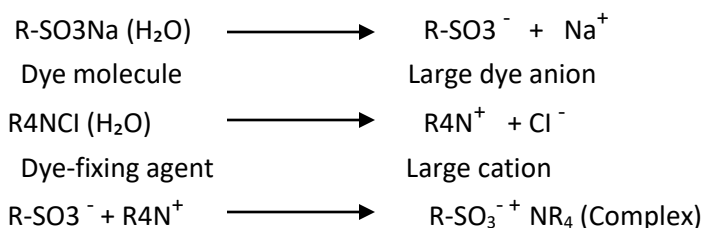
Formaldehyde (40%)   2-3% (owf)
Acetic acid (30%)   1% (owf)

The treatment is carried out at 60-70°C for 30 minutes followed by rinsing and drying.

3. Treatment with cationic dye fixing agents

Different types of dye-fixing agents are available for use in the after-treatment of direct dyed goods to bring about improved washing fastness properties; the light fastness, however, is impaired. These products are capable of ionising into long cations and small anions. On the other hand, direct dyes ionise into long anions and short cations. Thus, when solutions of these two are mixed, bigger complexes are formed as shown below.

$$R\text{-}SO3Na\ (H_2O) \longrightarrow R\text{-}SO3^- + Na^+$$
$$\text{Dye molecule} \qquad\qquad \text{Large dye anion}$$
$$R4NCl\ (H_2O) \longrightarrow R4N^+ + Cl^-$$
$$\text{Dye-fixing agent} \qquad\qquad \text{Large cation}$$
$$R\text{-}SO3^- + R4N^+ \longrightarrow R\text{-}SO_3^{-\ +} NR_4\ (Complex)$$

The mobility of the complex is much reduced; thus, the wet fastness of the dyed material is improved.

The treatment of the dyed goods with 1 - 2% (owf) of cationic dye-fixing agent is carried out at recommended temperature (varying for different products) for half an hour and this is followed by rinsing and drying.

4. Topping with basic dyes

Basic dyes do not have any affinity for cellulosic fibres. But special methods have been devised to apply them to cellulosic material as bright shades are obtained. The process involves the use of certain mordants, like tannic acid, which act as a bridge between the dye and the fibre as they have affinity for both cellulose and basic dyes. With direct dyed material the direct dye acts as the mordant and forms a complex when the material is treated with a solution of a basic dye. Such after-treatment of direct dyed material with basic dyes is generally referred to as "topping with basic dyes".

Topping with basic dyes is carried out in a cold bath containing a definite portion (half or even quarter) of the dye solution and the temperature is raised gradually to 60°C, and then adding the remaining dye portions at regular intervals. A small quantity of acetic acid (0.5 to 2%) is added to the dye bath for obtaining uniform shades. When all the basic dye has been added the treatment is continued at the same temperature for a further 45 - 60 minutes. This is followed by rinsing and drying.

5. Diazotisation and development of direct dyed goods

As discussed earlier, it is possible to enhance the wet resistance of water-soluble dyes by increasing the size of their dye molecules. Some of the direct dyes contain free amino (-NH$_2$) groups, which can be diazotised by chemical reaction with nitrous acid (HNO$_2$). The resulting diazonium salt is then treated with a coupling component, which results in the formation of an azo (--N-N-) group. The size of the direct dye molecule is now greatly increased and it will show good resistance to wet treatments.

The chemical reactions are shown below.
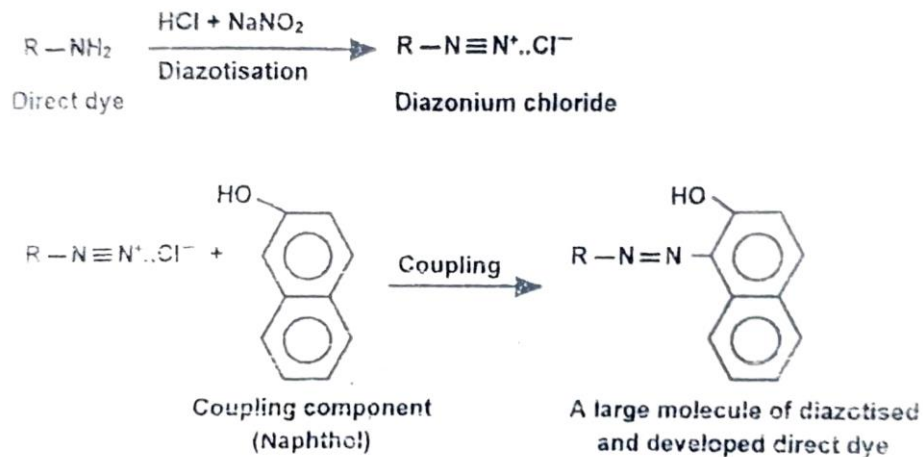
In practice, the direct dyed material is treated in the cold for 30 minutes in a bath containing

NaNO$_2$ **1-3% (owf)**
HCl   **5-10% (owf)**

The goods are rinsed and developed with a solution of the coupling component for 15-20 minutes. The material is then washed, soaped and dried.

5.52 Dyeing of cotton with Reactive dye.

Introduction

Stephen and Rattee, two textile chemists, were the first to show that certain dyes can chemically react with cotton fibre, forming covalent bonds and thus becoming part of the fibre itself. Before the advent of these reactive dyes it was not possible to achieve good fastness to hot wet treatments in cellulose dyed material, except in the vat class of dyes. Another unique feature of these dyes is the versatility of the application procedures, allowing them to be applied at temperatures ranging from ambient room temperatures to steaming methods, similar to those used for the continuous dyeing of vat and sulphur dyes. Since reactive dyes do not have the high degree of built in insolubility or a level of substantivity as high as direct dyes, dyes of small molecular size can be made. This allows leveling and dyeing to take place very rapidly compared with conventional dyes.

Since their introduction in the 1950s reactive dyes have shown rapid growth; even today, developments are taking place. The combination of brightness, fastness and ease of application associated with reactive dyes enables this class of dyes to be the major class of dyes used today to colour cellulosic fibres.

The structure of a reactive dye is shown below.
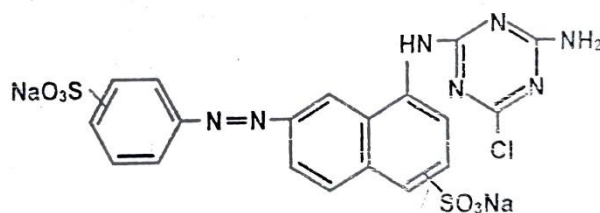
The above dye is a triazine reactive dye in which the chlorine atom is the reactive site.

Properties of Reactive Dyes

1. The reactive dyes, on account of the sulphonic acid groups in their molecules, are readily soluble in water.
2. Unlike direct dyes, the reactive dye molecules tend to be much less substantive to cotton and require much larger quantities of salt for exhaustion.
3. These dyes, unlike any other class of dyestuff, react and combine chemically (covalently) with cellulose. It is this characteristic that gives them the name "reactive dyes".
4. The reactivity of the dyestuffs can be reduced when desirable by blocking one of the reactive chlorine atoms, giving the hot-brand type of reactive dye.

5. Reactive dye molecules are not as long as those of direct dyes. Short molecules have two advantages namely, (a) clarity and brightness of hue and (b) easy penetration and therefore good leveling.

6. Textile materials coloured with reactive dyes have moderate to good light fastness and washing fastness.

7. Textile materials coloured with reactive dyes have to be thoroughly rinsed and soaped. Reactive dyes can react with the hydroxyl groups of the water molecule to produce dye molecules with poor substantivity for the fibre. In fact it is these molecules, which have to be removed by the washing-off process, involving soaping at the boil and rinsing. If these hydrolysed dyes are not removed, poor rubbing fastness will result.

8. The formation of the covalent bond between the dye and fibre occurs under alkaline conditions. The presence of acids may reverse this process. Perspiration and atmospheric pollution, which are both slightly acidic, may affect textile materials coloured with reactive dyes and result in some fading.

9. Reactive dyes can be applied to cellulosic fibres by the exhaust dyeing (batch dyeing), semi-continuous dyeing (pad-batch) and continuous dyeing techniques.

Classification of Reactive Dyes

Reactive dyes can be classified basically into three groups:

Group 1: Alkali-controllable dyes
Group 2: Salt-controllable dyes
Group 3: Temperature-controllable dyes

Group 1: Alkali-controllable dyes
Low-substantivity reactive dyes, often described as alkali-controllable dyes, exhibit rapid (easy) washing-off properties. Their level dyeing properties have to be regulated by slow (progressive) addition of alkali. This is done in order to encourage migration of dye to the substrate during alkali addition, and also to prevent the phenomenon of simultaneous exhaustion and fixation.

Group 2: Salt-controllable dyes
Medium-high substantivity reactivity dyes, often described as salt-controllable dyes, exhibit slow (poor) washing-off characteristics. Their level dyeing characteristics have to be controlled during the electrolyte addition stage. i.e. by portion-wise addition of salt.

Group 3: Temperature-controllable dyes
These dyes react with cellulose above the boil in the absence of alkali. They can be applied like Group 2 dyes, with alkali fixation being done, between 80 - 100°C. These dyes are self-leveling. Control of rate of temperature gives good results.

On the basis of the **reactive system**, reactive dyes can be further classified as follows.

(a) Monofunctional reactive dyes
(b) Bifunctional reactive dyes - these are further classified as homo-bifunctional and hetero-bifunctional dyes, as shown in the chart below.
(c) Multifunctional reactive dyes

```
                        ┌──────────────┐
                        │ Reactive Dye │
                        └──────────────┘
         ┌──────────────────────┼──────────────────────┐
┌─────────────────┐   ┌─────────────────┐   ┌─────────────────┐
│  Monofunctional │   │   Bifunctional  │   │  Multifunctional│
└─────────────────┘   └─────────────────┘   └─────────────────┘
                    ┌──────────┴──────────┐
            ┌─────────────────┐   ┌─────────────────┐
            │      Homo-      │   │     Hetero-     │
            │   bifunctional  │   │   bifunctional  │
            └─────────────────┘   └─────────────────┘
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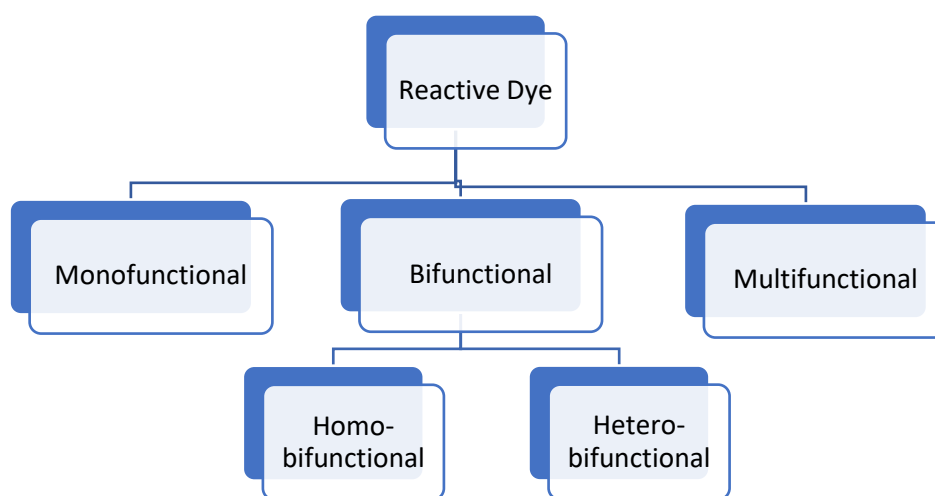
 (a) Monofunctional reactive dyes

These dyes are characterised by the presence of reactive groups (one or two reactive species) at individual locations in the dye molecule. All the reactive dyes developed during the early stages of development were monofunctional reactive dyes.

Typical examples of this kind are dyes having mono-chloro or di-chloro triazine or vinyl sulphone reactive groups. Although di-chloro triazine dyes contain two reactive chlorine atoms, located on the same triazine ring, they are considered as monofunctional reactive dyes.

(b) Bifunctional reactive dyes

These dyes have been introduced recently to the reactive dye range. They are characterised by the presence of two reactive groups of same type (mono or di-chloro triazine) or two different types (mono-chloro triazine and vinyl sulphone) at two different locations in the dye molecule. The bifunctional dyes are divided into two types.

i) **Homo-bifunctional** dyes having two reactive systems of the same type (triazine or vinyl sulphone)

ii) **Hetero-bifunctional** having two reactive systems of the mixed type (triazine-vinyl sulphone)

The various bifunctional combinations that can be formed are listed below.

MCT/MCT	monochlorotriazine/monochlorotriazine	(homo-bifunctional)
VS/VS	vinylsulphone/vinylsulphone	(homo-bifunctional)
MCT/VS	monochlorotriazine/vinylsulphone	(hetero-bifunctional)
FT/VS	fluorotriazine/vinylsulphone	(hetero-bifunctional)
FCP/VS	fluorochloropyrimidine/vinylsulphone	(hetero-bifunctional)

5.53 Dyeing of cotton with Vat dye.

Introduction

Vat dyes owe their name to the fact that the foremost member in this series, indigo, was applied to textiles by means of a fermentation process in wooden vessels commonly known as 'vat'. The dyes are amongst the oldest natural colouring matter derived from origins like vegetable (plants, stems, etc.), insects and animals.

Vat dyes provide textile materials with the best colour fastness of all the dyes in common use. The fibres most readily coloured by them are the natural and man-made cellulosic fibres, like cotton, viscose rayon, etc.

Properties of Vat Dyes

1. Vat dyes are insoluble in water.
2. They are generally converted to their soluble "leuco" state by means of sodium hydrosulphite (reducing agent) in the presence of caustic soda.
3. Vat dyes have excellent washing and light fastness.
4. Vat dyes are very expensive compared with the other classes of dye.
5. They are available commercially in different forms such as powder fine, microfine, ultra-disperse highly concentrated supra-paste and double-paste.

Classification of Vat Dyes

There are two different ways of classifying vat dyes. One is based on the **chemical constitution** of the dyes while the other is based upon their **methods of application**. The classification of vat dyes by chemical constitution is discussed in the following.

Classification by chemical constitution

(a) Anthraquinonoid vat dyes.
(b) Indigoid vat dyes
(c) Sulphurised vat dyes

(a) Anthraquinonoid vat dyes

The anthraquinonoid group covers a large range of shades. The dyes have good substantivity in water-soluble leuco form and display superior washing fastness properties. These dyes require a comparatively high concentration of alkali than the indigoid dyes and so, are not suitable for application to protein fibres. The chemical structure of an anthraquinonoid vat dye is shown below.

H$_3$CO   OCH$_3$

Br   Br

O   O
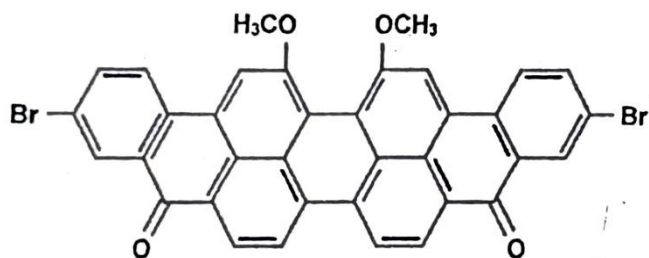
(b) Indigoid vat dyes

These dyes are characterised by the presence of the chromophore shown below.

O   O

C   C

C=C

NH   NH
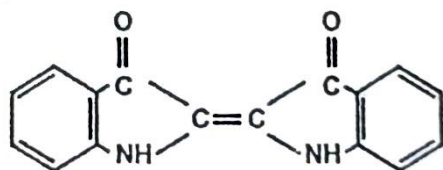
They are derivatives of either indigotin or thioindigo and form pale yellow solution under weakly alkaline condition.

Some of the vat dyes contain halogen derivatives of indigotin. For example, Tyrian purple, a natural dye is a dibromo derivative of indigotin. These dyes are widely used for dyeing blue denims.

(c) Sulphurised vat dyes

M/s Cassella (Germany) and Videl (UK) first manufactured these dyes under the respective brand names 'Hydron' and 'Redon'. These dyes have good all-round fastness properties, being intermediate to those of sulphur and vat dyes.

The dyeing method similar to that for vat dyes and the dye has to be chemically reduced using (caustic soda + sodium hydrosulphite + sodium sulphide) before dyeing. Hydron Blue is a classic example of this kind of dye.

Classification by method of application

Owing to the differences in sensitivity to process conditions and other properties, the vat dyes differ amongst themselves in respect of the following.

   i.   Ease of dissolution
   ii.   Affinity in the leuco-state
   iii. Rate of dyeing
   iv.   Dye-uptake
   v.   Requirement of electrolyte

vi.   Ease of re-oxidation
vii.   Sensitivity to reduction and oxidation, and
viii.   Stability to temperature and time during vatting and dyeing.

In the light of the factors mentioned above, each dyestuff in this group can be considered as a specific compound for which the process conditions during reduction, dyeing, oxidation and after-treatment are customised to its specific properties and behavior. However, for the sake of simplicity the vat dyes are classified into four groups on the basis of their methods of application, as shown in **Table** below.

Group	Vatting temperature (°C)	Dyeing temperature (°C)	Caustic soda (g/l)	Hydros (g/l)	Common salt (g/l)
IK	50	25-30	1.0-3.0	1.0 - 5.0	6.00 -50
IW	50	40 - 50	1.0 - 5.0	1.0-6.5	3.00 -25
IN	50 - 60	50-60	1.5 - 10	1.5 - 10	None
IN Special	Dyes require special conditions				

Table. The four groups of vat dyes

The IK (cold dyeing; K = kalt or cold in German) vat dyes are known for their optimum affinity at very low temperatures i.e. 20 - 30°C and require minimum additions of caustic soda and sodium hydrosulphite. The colour yield is greatly improved in the presence of larger amounts of salt.

The IW (warm dyeing) group of vat dyes is characterised by moderate caustic soda requirements. These dyes are vatted and exhausted at comparatively low temperatures i.e. 40-50°C. The dye baths are exhausted well in the presence of moderate concentrations of exhausting agent.

The IN (normal dyeing) group of dyes show their maximum affinity for cellulose at 60°C. These dyes require relatively high concentrations of caustic soda in the dyeing bath. The exhaustion of the dye bath is achieved even without the addition of common salt. However, these dyes require the use of retarding agents during dyeing because of their greater affinity for the fibre.
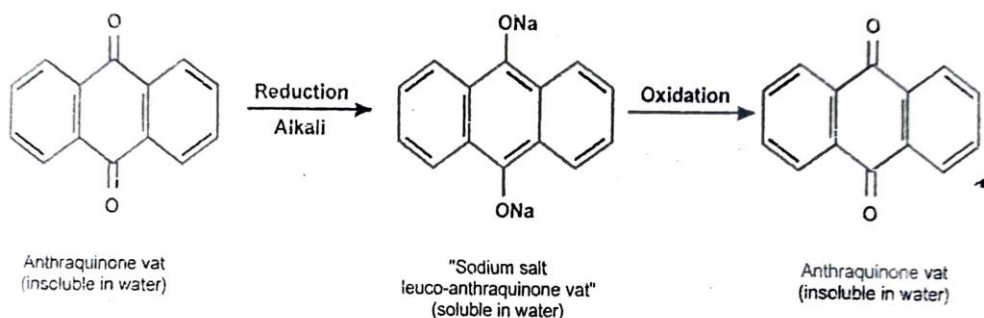
IN-Special dyes or simply IN-Spl dyes (special dyeing dyes), the fourth group of vat dyes includes specific dyes like blacks, which require relatively higher concentrations of caustic soda, sodium hydrosulphite and also much higher vatting and dyeing temperatures.

Chemistry and Application of Anthraquinonoid (AQ) Vat Dyes

The anthraquinone class recognised and made famous first by the ICI trade name "Caledon" is the most important class of vat dye for cotton dyeing. It is easily the largest class and most of its members possess high all-round fastness. They are characterised by the possession of at least two quinonoid carbonyl groups, that is, the carbonyl groups are a part of benzene rings. Under alkaline conditions of chemical reaction, anthraquinone, on reduction can give not one, but several products.

Like the other classes of vat dyes, the AQ vat dyestuffs are insoluble, coloured compounds which can be easily converted to a soluble form that is substantive to cellulose. These dyestuffs contain two or more carbonyl groups, C=O which are easily reduced in alkaline solution to the 'leuco' form,C-O-H and then to its sodium salt C-ONa, which is soluble; the insoluble colour is then regenerated in the fibre by oxidation. The changes are explained by the following representation.

When anthraquinone (AQ) vat dyestuffs are reduced, a marked change in colour of the reduced solution usually occurs, e.g. the leuco compound of an AQ vat yellow dye is blue and that of an AQ vat orange dye is red-violet; the AQ vat green dye reduces to a blue solution. However, the AQ blue vat dyes are an exception in this respect, showing only slight changes in shade from blue to slightly greenish (or yellowish) blue on reduction to their leuco-compounds. Some practice and experience is required to clearly identify whether complete reduction of these dyes has taken place or not. The changes described in general for vat dyes are shown below with specific reference to the anthraquinone vat dye.

Anthraquinone vat
(insoluble in water)

"Sodium salt
leuco-anthraquinone vat"
(soluble in water)

Anthraquinone vat
(insoluble in water)

or simply, with reference to the central benzene ring, as follows:
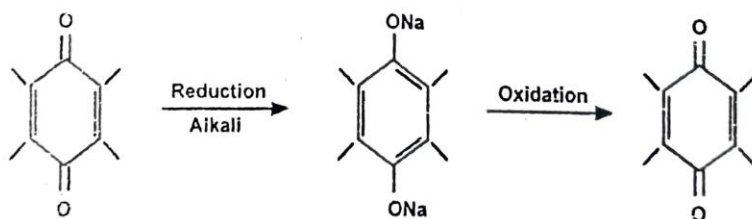
Application of vat dyes

The application of vat dyes to cotton goods involves the following four basic steps.

1. Vatting

This step achieves the conversion of insoluble commercial vat dye powder into its soluble sodium salt.

2. Dyeing

This step brings about absorption of the reduced and dissolved vat dye by the fibre from an alkaline reducing bath in the presence of exhausting or retarding agent.

3. Oxidation

The soluble sodium salt of leuco vat dye absorbed by the fibre is converted into its original insoluble form. This may be done either by air or chemical oxidation.

4. After-treatment

The dyed material is subjected to a treatment with boiling detergent solution to get the proper shade (hue) with brilliance and good fastness properties.

5.54 Dyeing of cotton with Azoic dye.

Introduction

Azoic dyes are not ready-made dyes but are produced within the substrate using two different components i.e., **naphthol's and bases**, which are also referred to as **"coupling components"** and **"diazo components"** respectively. Owing to the requirement of very low temperatures requiring the use of ice in the application of azoic dyes, this group of dyes is also known as **"ice colours"**.

The coloured pigment formed by the chemical combination of the two colourless - components is insoluble in water and therefore exhibits extremely good fastness to wet treatments. The insoluble dye is a product of a reaction between water-soluble components in an aqueous medium; this contributes to the occurrence of the reaction in the solution phase also. The pigment formed in the bath is loosely deposited on the surface of the material and leads to poor rubbing fastness. However, the dyeing process aims at the production of the insoluble azoic pigment within the fibre structure. It is for this reason that azoic dyes are classified as **"ingrain dyes"**.

Properties of Azoic Dyes

The azoic dyes are characterised by the following properties.

1. They are insoluble in water.
2. They are not ready-made dyes. The colour is formed in the fibre by two components usually referred to as naphthol's and bases.
3. The dyed goods have very good to excellent light fastness.
4. The dyed goods have good washing fastness.
5. The dyed goods suffer from poor rubbing fastness and this can be overcome by proper soaping treatment.

Application of Azoic Dyes to Cotton

The steps involved in dyeing cotton material are stated below.

1. Impregnation with a solution of naphthol. This step is called **'naphtholation'.**
2. Development of the chromophore (azo group). This is the **'diazotisation'** step.
3. Development of coloured pigment. This is the **'coupling'** step.
4. Removal of the surface colour from the dyed fibre. This step is called **'soaping'**.

The chemical equations involved in the first three steps are shown in **Figure.**
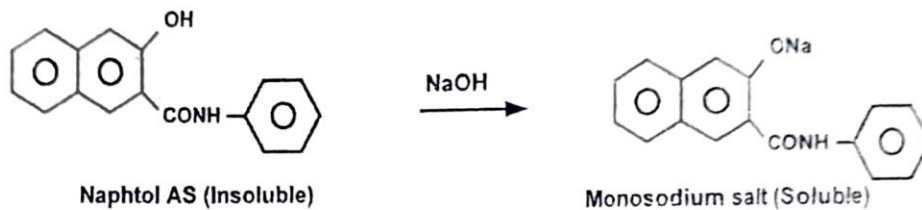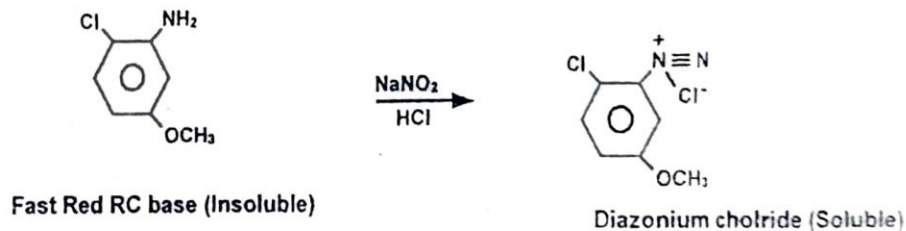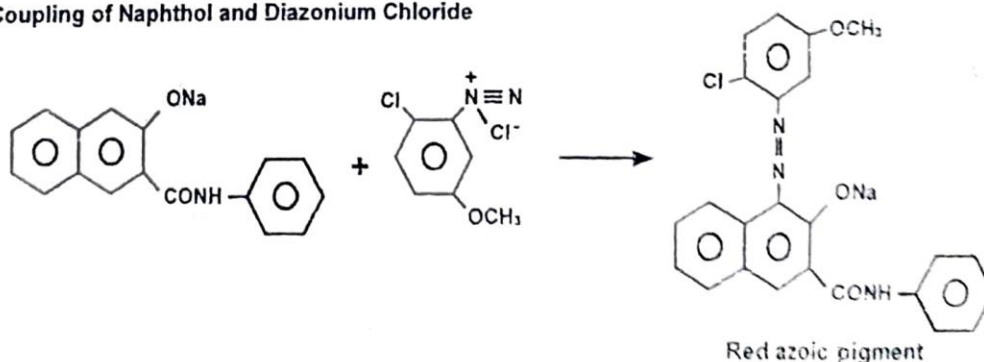
Figure. Chemical reactions in the formation of an azoic dye

1. Naphtholation

i) Preparation of the naphthol solution

Naphthols are insoluble in water. They can be dissolved in water by converting them into sodium compounds, which are soluble in water. For this caustic soda is used.

Naphthol -- OH + NaOH $\longrightarrow$ Naphthol -- ONa

Insoluble in water   Sodium salt of the naphthol

                                      soluble in hot water

ii) Impregnation with naphthol solution

Treat the scoured/bleached material with naphthol solution at room temperature for 20 to 30 minutes. In some cases, the addition of common salt or Glauber's salt increases the absorption. Squeeze the naphtholated goods evenly, so as to leave it uniformly naphtholated.

2. Development of chromophore (azo group) - diazotisation

Dissolution of the base

Bases are insoluble in water. They should be converted into water-soluble salts (i.e. hydrochloride of the base) using concentrated hydrochloric acid.

$$\text{Base - NH}_2 + \text{HCl} \longrightarrow \text{Base NH3}^+ \text{Cl}^-$$

Water-insoluble base   **Hydrochloride of the base soluble in warm / hot water**

Diazotisation of the base

The reaction between the hydrochloride of the base with nitrous acid occurs best at low temperature (0°-5°C) in around 20 - 30 minutes and is called diazotisation of the base. This is carried out by adding sodium nitrite to the hydrochloride of the base in the presence of hydrochloric acid. At this stage the base is converted into diazonium chloride, which is also called diazonium salt.

The reaction steps in diazotisation are given below.

i. $\text{HCl} + \text{NaNO2} \longrightarrow \text{HNO}_2 + \text{NaCl}$
Nitrous acid

ii. $\text{Base-NH3}^+ \text{Cl}^- + \text{HNO}_2 \longrightarrow \text{Base- N=N} + 2\text{H}_2\text{O}$
                                                   |
                                                   Cl

The --N=N- group is called the "azo" group.

Neutralisation

The diazotised base in this state will be highly acidic due to the excess hydrochloric acid in it. Good coupling will take place with naphthol only if its pH is reduced to the range 5 - 6. Sodium acetate is added to the diazotised base liquor to convert the excess hydrochloric acid into acetic acid.

$$\text{HCl} + \text{CH}_3\text{COONa} \longrightarrow \text{CH3COOH} + \text{NaCl}$$

Coupling will also be slowed down if the liquor becomes alkaline and this can occur easily on account of the caustic soda brought into the liquor by the naphtholated yarn. This excess of alkali can be neutralised by adding an alkali-binding agent, e.g., aluminum sulphate.

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$$

Aluminium	Aluminium	Sulphuric
sulphate	hydroxide	acid

$$2NaOH + H_2SO4 \longrightarrow Na_2SO4 + 2H_2O$$
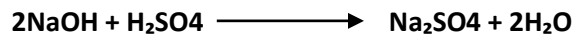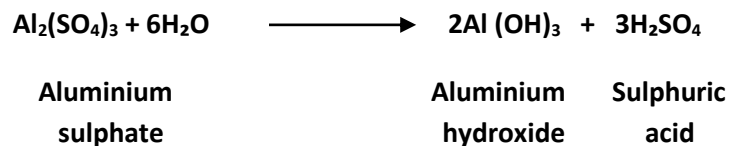
The addition of neutralising and alkali-binding agents must be done just before the developing step.

3. Developing of coloured pigment - coupling

The naphtholated material is entered and developed in the base solution for 15-20 minutes at room temperature. This process is called coupling or developing. The pH should be maintained around 5 to 6 during this step.

Formation of insoluble azoic pigment or developing

Naphthol – Ona + Base-N=N-Cl $\longrightarrow$ **Naphthol** $\begin{smallmatrix} ONa \\ \diagup \\ \diagdown \\ N=N\text{-Base} \end{smallmatrix}$ **+ HCl**
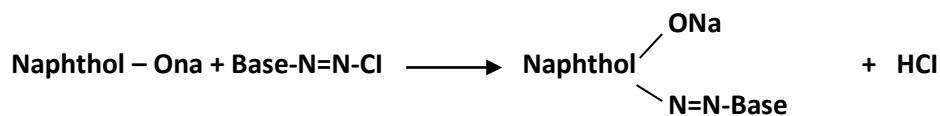
Insoluble azoic pigment

4. Removal of surface colour - soaping

After dyeing, the material is rinsed in cold water to which 1 g/l hydrochloric acid is added, and then it is soaped at the boil for 30 minutes to remove unfixed dyes (surface dyes).

5.55 Dyeing of cotton with Sulphur dye.

Introduction

Sulphur dyes being relatively inexpensive are widely used for dyeing of cellulosic fibres and their blends especially with polyester/cotton yarn is dyed in a package or hank dyeing machine. Sulphur dyes are widely used for black, blue, maroon, olive and green colours in medium to heavy depths.

Fastness properties of sulphur dyes vary markedly throughout the range, e.g., light fastness of yellow dyes is almost 3 whereas black is about 7. Wash fastness is generally good. Fastness to bleaching is poor except in the case of a few dyes. These dyes are available in powder, pre-reduced powder, grains, paste and liquid form.

Properties of Sulphur Dyes

1. Sulphur dyes are insoluble in water.
2. They are soluble in a solution of sodium sulphide to which sodium carbonate may or may not be added.
3. The sodium sulphide acts as a reducing agent, severing the sulphur linkage and breaking down the molecules into simpler components, which are soluble in water.
4. The wash fastness is good (3-5) and the light-fastness is satisfactory (3-7). These dyes have poor fastness to chlorine.

Classification of Sulphur Dyes

The sulphur dyes can be classified into the following groups

1. Sulphur dyes
2. Leuco sulphur dyes
3. Solubilised sulphur dyes
4. Condensed sulphur dyes

1. Sulphur dyes

These are water insoluble dyes, normally applied in alkaline-reduced (leuco) form. Sodium sulphide is normally used as reducing agent, and after dyeing, the dye is oxidised back into its original insoluble form in the fibre.

2. Leuco sulphur dyes

These are powders or liquid-based dyes containing the soluble leuco form of the parent dye. A reducing agent, usually sodium sulphide or hydrosulphite, is used in Dyeing-Water Insoluble Dyes - Sulphur Dyes

sufficient quantity to make the dye suitable for application either directly or with the addition of only small amount of extra reducing agent.

3. Solubilised sulphur dyes

These are thiosulphuric acid derivatives of the parent dyes, and are non-substantive to cellulose but are converted to substantive alkali soluble thiol form during dyeing.

4. Condensed sulphur dyes

These are sodium-S-alkyl or S-aryl thiosulphates. They do require sodium sulphide for dyeing, but conventional sulphur dyeing methods are unsuitable for them.

Chemical Reactions in Sulphur Dyeing

The chemical reactions in sulphur dyeing are explained in the following. The insoluble dye is converted to smaller soluble components called thiols by the reducing agent.

$$\text{Dye.S--S. Dye} \ + \ 2H \ \longrightarrow \ \text{Dye.SH} \ + \ \text{HS. Dye}$$

Insoluble	Reducing	(Thiols)
sulphur dye	agent	Smaller components
		of dye soluble in water

The thiols, containing the SH group are readily oxidised in the fibre to the original insoluble sulphur dye, giving a colour with very good wash fastness.

$$\text{Dye.SH} \ + \ \text{HS. Dye} + \ O \ \longrightarrow \ \text{Dye.S --- S. Dye} \ + \ H_2O$$

Water soluble or	Original insoluble
Leuco form of the	sulphur dye molecule
sulphur dye molecule	

Application of Sulphur Dyes to Cotton

The dyestuff (usually 5 to 25% owf) is pasted with soda ash and sodium sulphide. The quantity of soda ash is equal to the amount of dyestuff taken and the sodium sulphide is between half and twice the weight of the dye. Add sufficient quantity of hot water to the paste and if necessary, boil it; then filter the dye solution to remove insoluble impurities.

Dyeing

Maintain the temperature of the bath at the boil. Enter the goods in the dye liquor and add common salt or Glauber's salt (from 10 to 50% owf). The amount will vary according to the depth of shade. The salt should be added in portions while keeping the bath temperature at the boil.

Steps in dyeing

The steps in the dyeing of cotton yarn in hank form with sulphur dyes are shown clearly in **Figure.**

Scoured / Bleached yarn
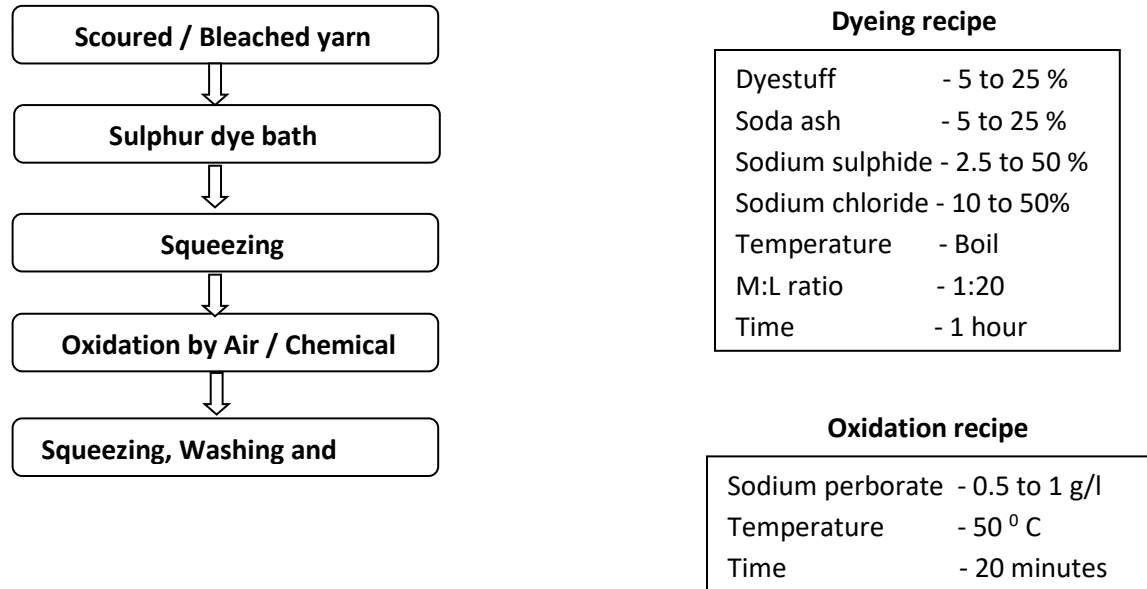
⇩

Sulphur dye bath

⇩

Squeezing

⇩

Oxidation by Air / Chemical

⇩

Squeezing, Washing and

Dyeing recipe

Dyestuff	- 5 to 25 %
Soda ash	- 5 to 25 %
Sodium sulphide	- 2.5 to 50 %
Sodium chloride	- 10 to 50%
Temperature	- Boil
M:L ratio	- 1:20
Time	- 1 hour

Oxidation recipe

Sodium perborate	- 0.5 to 1 g/l
Temperature	- 50 ^{0} C
Time	- 20 minutes

Figure. Steps in sulphur dyeing

Dissolving sulphur dyes

The dyestuff is pasted with soda ash and sodium sulphide. 2 g/l of soda ash will normally be adequate. The quantity of sodium sulphide is usually twice the weight of the dye. Boiling water is then added to the paste until the dye dissolves. Strain the dissolved dye before it is added to the dye bath.

Dyeing

The dye bath is made up with dyestuff and 5 to 25 percent of the weight of the goods of common salt or 10 to 50 percent of crystalline Glauber's salt, the actual amount varying according to depth of shade. The salt may be added at the commencement, but if there is any risk of uneven dyeing it is preferable to add it after the temperature has reached 100°C, and that too in several portions. The addition of a surface-active penetrating agent is recommended. With most sulphur dyes the liquor is brought to the boil and dyeing continued in a cooling liquor for a further half an hour.

Oxidation step

Since some sulphur dyes oxidise slowly, it is better to wait for the true shade to develop. The procedure is to run them, after rinsing, in a solution sodium perborate of 0.5 to 1 g/l concentration, at 40 to 50°C for 20 minutes.

Soaping

The process is important for removing superficial dyestuff and traces of free sulphur from the fabric. The washing and rubbing fastness properties of the dyed goods are also improved. Soaping is carried out in a bath containing 2-4% soap solution at the ` boil for 20-30 minutes. The goods are washed thoroughly with hot and cold water respectively.

After-treatment

The washing and light fastness of the sulphur dyes can be improved by using one of the following after-treatments.

i) Treatment with metallic salts e.g., dichromate's and copper sulphate either alone or in combination.

ii) Topping with basic dyes.

i) Treatment with metallic salts

Quite similar to direct dyes, the light fastness of sulphur dyed goods can be improved by treating the goods with copper sulphate in the presence of acetic acid; the washing fastness is enhanced by treatment of the dyed goods with dichromate and acetic acid. The process consist of treating the dyed goods in a bath containing:

$$K_2Cr_2O_7 \qquad 1 - 2.0\%$$
$$CuSO_4 \qquad 1 - 2.0\%$$
$$\text{Acetic acid} \qquad 1 - 2.0\%$$

for 20-30 minutes at 70°C followed by thorough washing in hot and cold water respectively.

ii) Topping with basic dyes

Again, similar to direct dyes, sulphur dyes possess a great affinity for basic dyes and act as a mordant. (Basic dyes as such do not have any affinity for cellulosic goods). Hence cotton goods dyed with sulphur colours can be topped with basic dyes so as to get enhanced brilliance of shade and improved washing fastness properties as well. However, the light fastness is impaired.

The process of topping involves thorough washing of the dyed goods to ensure complete removal of sodium sulphide and traces of alkali. The material is then dyed in a bath containing basic dye and 3-4% acetic acid (60%) at 60 - 70°C for a period sufficient to get complete exhaustion. Apart from reducing the light fastness the treatment also changes the tone of the sulphur dyed shade.

Disadvantages of Sulphur Dyes

The major disadvantages associated with use of sulphur dyes are,

i) Bronziness of shades
ii) Tendering of sulphur black dyed goods.

i. Bronziness of shades

This is one of the common faults, especially with sulphur black. There are various causes of bronziness; some of them are listed below.

1. Presence of dyestuff on the material, because of dyeing in a strong bath.

2. Use of excessive quantities of common salt during dyeing.

3. Excessive delay in washing after draining the dye liquor or lifting off the goods from the dye bath.

4. Insufficient quantity of sodium sulphide present during dyeing and resulting in incomplete dissolution of dyestuff. Dye builds up on the surface of the material being dyed and gives rise to bronziness because the superficial dye is quickly oxidised to insoluble form on the surface itself.

In spite of all precautions, if bronziness appears, it may be reduced by any of the following treatments.

i) The dyed material is treated in a bath containing a strong solution of sodium sulphide (i.e. 2-4%) at 60-70°C. The treatment removes excess of dye from the surface of the material and thus bronziness is overcome.

ii) In another treatment, the goods are treated with liquor ammonia 1 - 2 ml/l and 2-3 g/l TRO at 40 - 50°C for 30-45 minutes.

iii) The bronziness can also be removed by treating the dyed material in a boiling soap solution for sufficient periods.

iv) Treatment of dyed goods with olive oil emulsions containing soda ash also removes the bronziness. The goods are hydro-extracted and dried without washing.

ii. Tendering of sulphur black dyed goods

Cotton goods dyed with sulphur black suffer from the serious drawback that they get degraded on prolonged storage. The degradation or tendering results in fabric strength loss. The degraded material has been found to contain free sulphuric acid. The formation of sulphuric acid has been attributed to free sulphur present in the goods, which on exposure to the moisture in the atmosphere gets converted to sulphuric acid. The acid hydrolyses the cellulose and results in the degradation of the material.

It has been observed that the presence of iron the dyed material accelerates the degradation of cellulose and also the decomposition of the dye itself. Iron as an impurity may be acquired from the sodium sulphide used in dyeing. Also, cotton material dyed with sulphur black is found to have an increased tendency to get tendered when they are after-treated with copper sulphate.

Treating the dyed material with potassium or sodium dichromate, followed by rinsing, can reduce the danger of tendering on storage. Free and active sulphur is oxidised and the oxidation products are removed before storage. Alternatively, an alkaline finish (with soda ash or other mild alkalies like sodium acetate, tetrasodium phosphate) may also be used as a precautionary measure, the treated goods being dried without washing or rinsing. In this case any acid formed during storage, will be neutralised by the alkali present in the dyed material.

5.55 Dyeing of Silk and Wool with Acid dye.

Introduction

Most acid dyes are sodium salts of organic sulphonic acids. They consist of an aromatic structure containing a chromogen and a solubilising group, which is almost always a sulphonic acid salt (D-SO3Na) The acid dyes, are soluble ionic compounds where the colour is contained in the anionic portion.

Initially acid dyes were called so because the presence of an acid was required in their application. The term 'acid dyes' is also consistent with their chemical structure since they are salts of organic acids. Often, acid dyes are also referred to as 'anionic' dyes.

Acid dyes are used mainly for both natural protein fibres (wool and silk) and the synthetic polyamide fibres (nylon). These dyes are also used occasionally for the dyeing of other fibres such as the acid-dyeable acrylic fibre. The chemical structure of an acid dye shown in **Figure.**
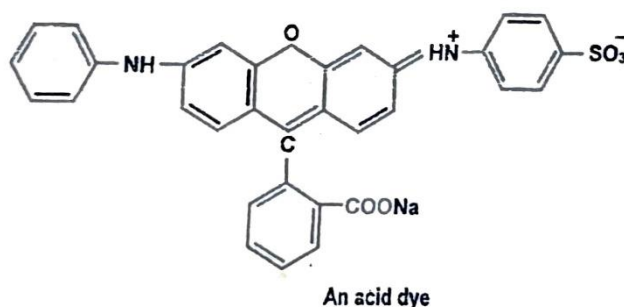
An acid dye

Properties of Acid Dyes

1 Acid dyes produce a wide range of brilliant shades.

2. They do not have any affinity for cellulosic fibres.

3. They have a good affinity for protein and polyamide fibres and are the main class of dyes used for wool, silk and nylon dyeing.

4. Individual dyes of this class vary in terms of their fastness properties and hence care should be taken while dyeing mixture shades.

5. The rate of dyeing of acid dyes is a function of temperature and each member has a specific temperature at which its rate of dyeing and exhaustion are maximum.

6. Chemically, acids dyes resemble the direct dyes in the sense that after dissolution they produce a coloured anion (DSO_3^-) and a colourless cation (Na^+). They are generally represented as D-SO$_3$Na, where the 'D' represents the chromogen part of the dye molecule.

Classification of Acid Dyes

The acids dyes are organic acids in which the acid group is generally sulphonic acid ($-SO_3H$) and in some cases carboxylic ($-COOH$). The free acids are hygroscopic in nature and are difficult to separate from their solutions; it is for this reason that acids dyes are manufactured as sodium salts. There are different ways of classifying acids dyes as indicated below.

i) Classification by state of division i.e. size of dye molecule

ii) Classification by the concentration of acid used in the dyeing bath

iii) Classification by the migration and fastness properties of the dyes

With respect to their state of division, acid dyes are broadly classified into the following two groups:

1. Molecularly split acid dyes and

2. Aggregated acid dyes.

1. Molecularly split acid dyes

These dyes are known by their tendency to give clear aqueous solutions. The individual molecule is ionised when dissolved in water.

$$D\text{-}SO_3Na \longrightarrow DSO_3^- + Na^+$$

These dyes are applied from baths containing sulphuric or formic acid, and in the absence of the acid they show poor affinity for protein fibres. Because of the splitting in water, the dyes exhibit good migration properties and so any uneven dyeing in the initial stages of dyeing can be easily corrected by continuing the dyeing at the boil. These dyes lack fastness to wet treatments such as washing and milling.

2. Aggregated acid dyes

These dyes, when dissolved in water, do not split into individual molecules. The dye molecules join together to from clusters or aggregates. However, some of the molecules get ionised to produce charged aggregates. Owing to their limited solubility, their solutions are turbid. Increase in temperature, however, results in increasing ionisation. When these dyes are applied to cotton or other cellulose fibres in a neutral bath, they stain the fibres. They have high affinity for polyamide and protein fibres, the affinity increasing further with the addition of acid to the dye bath. The aggregation of molecules results in poor leveling and migration properties. However, the fastness to wet treatments is comparatively good.

In another method of classification, acid dyes are classified into the following three classes depending on their fastness **properties and concentration of acid used** in the dye bath.

a. Leveling acid dyes
   b. Milling acid dyes
   c. Super milling acid dyes

Leveling acid dyes

As the name indicates, these dyes have higher leveling properties. Practically, they correspond to molecularly split dyes as their fastness to wet treatments is not satisfactory, but their light fastness is good. While producing mixture shades, the light and washing fastness of the individual components should be taken into account. These dyes are applied from a bath containing sulphuric acid or formic acid and so are sometimes called 'strongly acid' dyes. During their application if unevenness is observed, it may be corrected by a prolonged boiling of the dye bath.

Milling acid dyes

These dyes lack in brightness and levelling properties when compared with the levelling acid dyes. They have better washing fastness properties and also withstand milling treatments. The dyes are generally applied from a bath containing acetic acid and therefore are sometimes referred to as 'weakly acid' dyes.

Super milling acid dyes

These are also called neutral dyeing dyes, since they are applied from neutral baths. They do not give true solutions but produce colloidal solutions, which break up on boiling. Their migration/leveling power is negligible but washing and light fastness is generally good.

The general **characteristics** of acid dyes are summarised in **Table**

Characteristics	Leveling Acid dyes	Milling Acid dyes	Super milling Acid dyes
Chemical added to dye bath	Sulphuric acid	Acetic acid	Ammonium acetate
pH of the dye bath	2-4	4-6	6-7
Leveling property	Good	Moderate	Very poor
Fastness to wet treatments	Poor	Good	Very good
Molecular weight	Low	High	High
Solubility in water	High	Low	Low
State of division in	Molecularly split	Colloidal(aggregates)	Colloidal(aggregates)

water			
Affinity to nylon, silk & wool	Low	High	High

Mechanism of Acid Dyeing of Protein Fibre

Practically speaking, protein fibres have affinity for all classes of synthetic dyes. However, certain dye classes cannot be used for dyeing them e.g. sulphur dyes, which are not suitable because of the use of sodium sulphide. Similarly, dyes like naphthol, vat, etc., are not used as they require strong alkali which is injurious to protein fibres. Direct and basic dyes are used to a limited extent because of their poor fastness properties. The dyeing of wool and silk is similar in practical terms because of the fact that both have affinity for dyestuffs. The major difference arises from the fact that the dyeing of silk takes place at comparatively lower temperatures.

Acid, mordant and metal-complex or pre-metalised dyes are the most-frequently used classes of synthetic dyes for wool, silk and nylon. These dyes produce a variety of brilliant shades. The mechanism of dyeing these fibres is explained in the following.

Wool is composed of keratin, which is made up of different amino-acids arranged in the crystalline and amorphous regions of the fibre. Wool can be represented in its simplest form as shown below.

$$NH_2 \text{---W--- COOH}$$

When dipped in water the H^+ from the carboxylic ion is transferred to the amino group at the other end so that the two ends become electrically charged, as indicated below
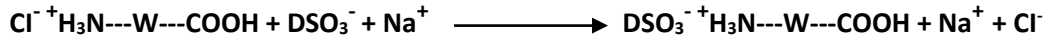
$$NH_3 \text{---W---COO}^-$$

When a protein fibre containing such electrically-charged molecular ends is entered in a solution of an acid, say HCl, some of the negatively charged carboxylate group take up H^+ ions from the solution and become electrically neutral and the Cl^- anions from the acid are absorbed by the positively charged amino end groups in the protein.

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$NH_3\text{---W---COO}^- + H^+ + Cl^- \longrightarrow Cl^- {}^+H_3N\text{---W---COOH}$$
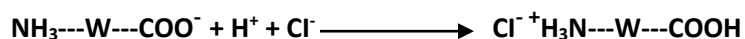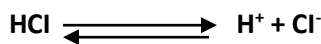
It is clear from the above that when wool is entered in a solution of acid, the concentration of acid decreases with the formation of positive sites in the protein macromolecules. An acid dye, designated as D-SO$_3$Na, splits into its ions when dissolved in water, as indicated below:
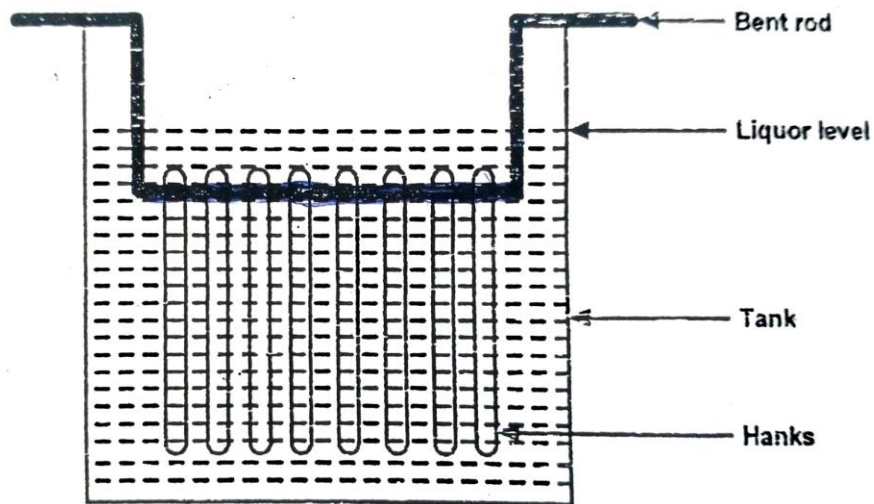
$$D\text{-SO}_3Na \longrightarrow DSO_3^- + Na^+$$

$$Cl^- \, {}^+H_3N\text{---}W\text{---}COOH + DSO_3^- + Na^+ \longrightarrow DSO_3^- \, {}^+H_3N\text{---}W\text{---}COOH + Na^+ + Cl^-$$

5.6 Working principles of Winch, Jet, Beam, Hank and Package dyeing machine, Jigger, J-Box
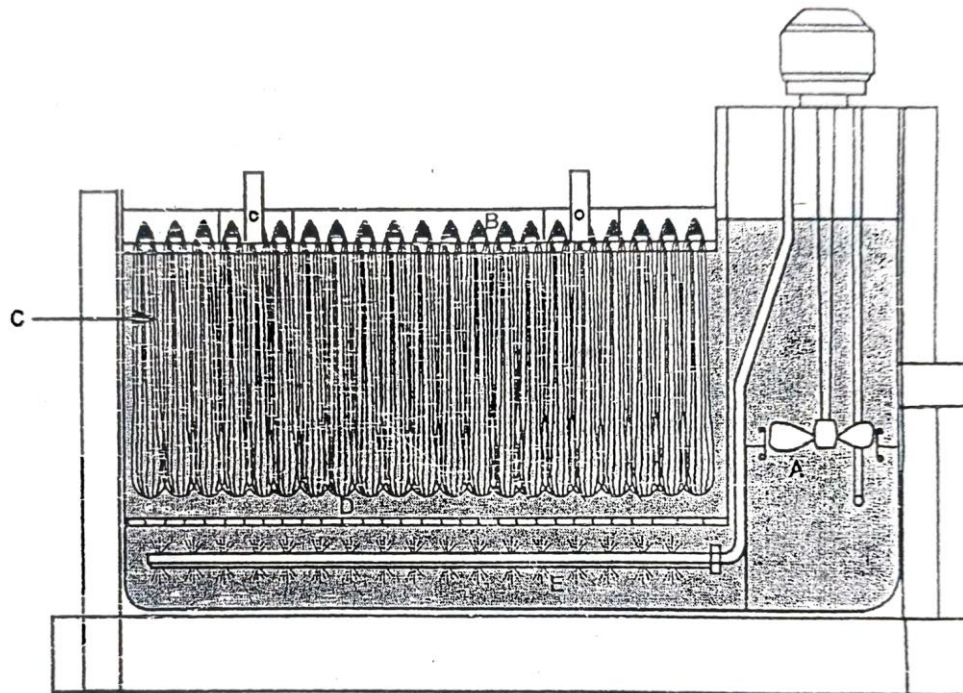
Hank Yarn Dyeing Machines

(a) **Open beck dyeing**

Bent rod for suspending the hanks in an open beck dye bath

I.   The beck is a large stainless-steel tank provided with a water inlet.
II. Provision is made to heat the dye liquor. Heat is usually generated under the tank by burning a suitable fuel. The tanks contain the dye liquor and a number of hanks suspended on flat stainless-steel rods are made to dip in the bath and periodically are rotated manually.
III. Two operatives standing on either side of the tank lift each rod bearing a number of hanks and invert the position of the hanks with the help of another rod and then dip the hanks in the dye liquor.
IV. When straight flat rods are used for supporting the hanks, the rods rest on the sides of the tank, so some portions of the hanks are always above the liquor level. This could lead to uneven dyeing.
V.   However, in actual practice, the hanks are reversed at regular intervals and unevenness can be avoided.

(b) Automated beck type machine

A - Impellor   D - False bottom
B - Hank rods   E - Steam pipe
C - Hanks

Hussong hank yarn dyeing machine

I.   One of the oldest automated hank yarn machines is the Hussong machine, it consists essentially of a frame carrying poles on which the hanks are hung and which can, when loaded, be lowered into a rectangular vessel containing the dye liquor.
II.   The liquor is circulated by means of an impellor, which is kept away from the yarn by a partition. When the impellor rotates, it pushes the dye liquor down and into the main yarn compartment through a perforated false bottom located below the suspended hanks of yarn.
III. To distribute the flow of dye liquor uniformly, the holes in the false bottom are arranged such that there are a greater number of holes at the end remote from the impellor than adjacent to it. The false bottom also serves to separate the steam pipe from the yarn. The impellor rotates in opposite directions alternatively so that the circulation is either from below

(c) Cabinet dyeing machine

A - Heat exchanger
B - Continuous liquor cooling
C - Impellor
D - Tank
E - Static pump
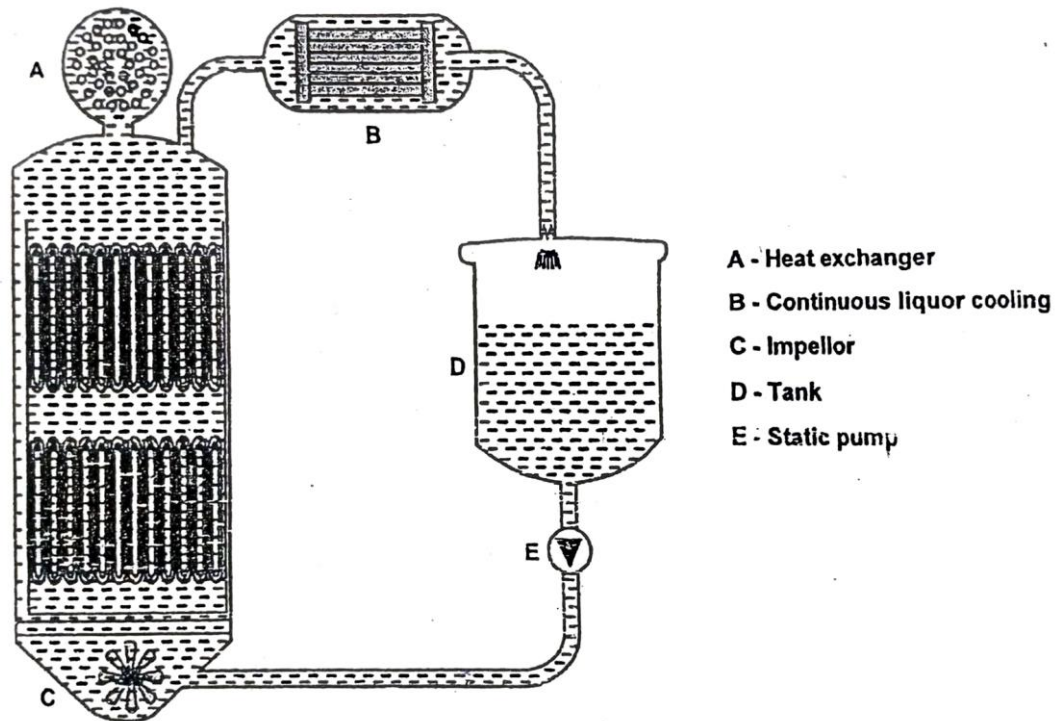
‹ Cabinet dyeing machine

I.   Cabinet dyeing machines are used for dyeing yarn in hank form.

II. In the cabinet, the hanks hang on oval sticks in two or four compartments and the liquor is circulated through them by means of a special reversible propeller, which is located at the lower part of the main chamber of the machine.

III. The drive from the electric motor is transmitted by means of V-belt and pulleys, which permit the selection of different speeds in order to suit the circulation of the liquor for the count and quality of the yarn.

IV. Reversal of the flow of liquor can be effected automatically by means of a special cyclic device with pre-selection of times.

V.   An automatic temperature controller for use with or without preprogrammed controller or a completely computerised programme with all pneumatically activated valves for fully automatic operation are available.

VI. Devices for heating and distribution of the liquor are also fitted in the lower part of the cabinet. The sampling device with a stainless-steel safety valve is fitted in a most accessible position and enables sampling to be performed very easily and safely. Provision is available in this machine

for different spacings of the hank rods, making them suitable for different reeling lengths and types of yarn.

VII. Hydrostatic pressure and static pressure models are available for working temperatures up to 100°C and 108°C respectively.

VIII. The M: L ratio is normally 1:15 or 1:20 depending upon the hank size. Cabinet hank dyeing machines are available for dyeing hanks in three sizes of 54", 72" and 90".

IX. Cabinet dyeing machines are available as single-tier and double-tier models.

X. Single-tier machines are available for dyeing in capacities of 50 kg and 75 kg for cotton yarn. Double-tier machines are available for dyeing in capacities of 100 kg, 200 kg and 500 kg of cotton yarn.
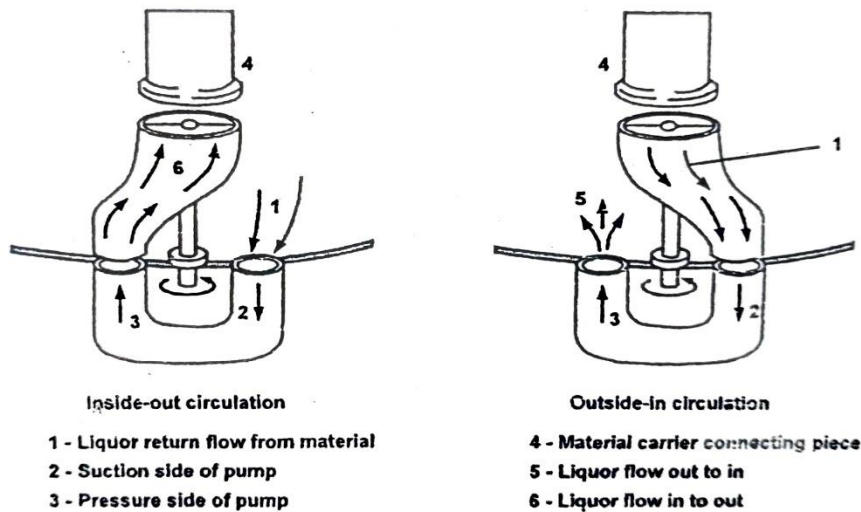
Yarn package dyeing machine
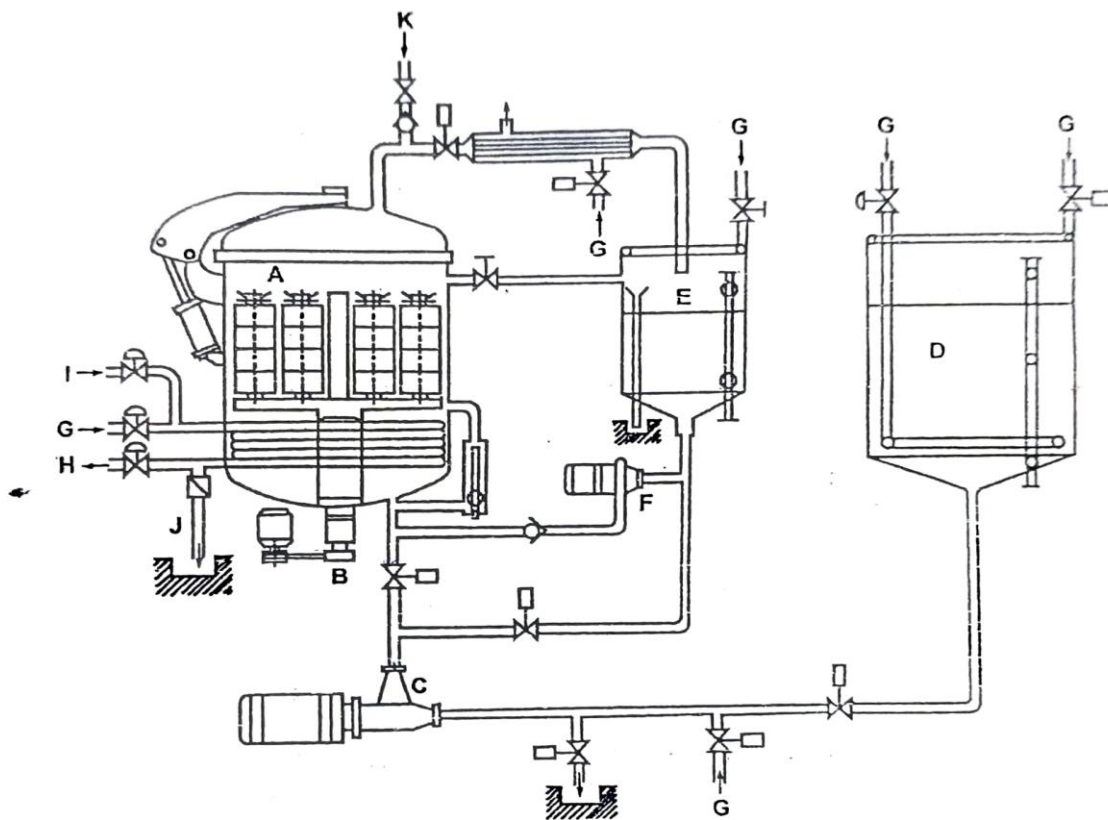
A - Dyeing vessel   G - Water
B - Turbo pump   H - Hot water
C - Transfer pump   I - Steam
E - Expansion vessel   J - Condensate
D - Stock tank   K - Compressed air
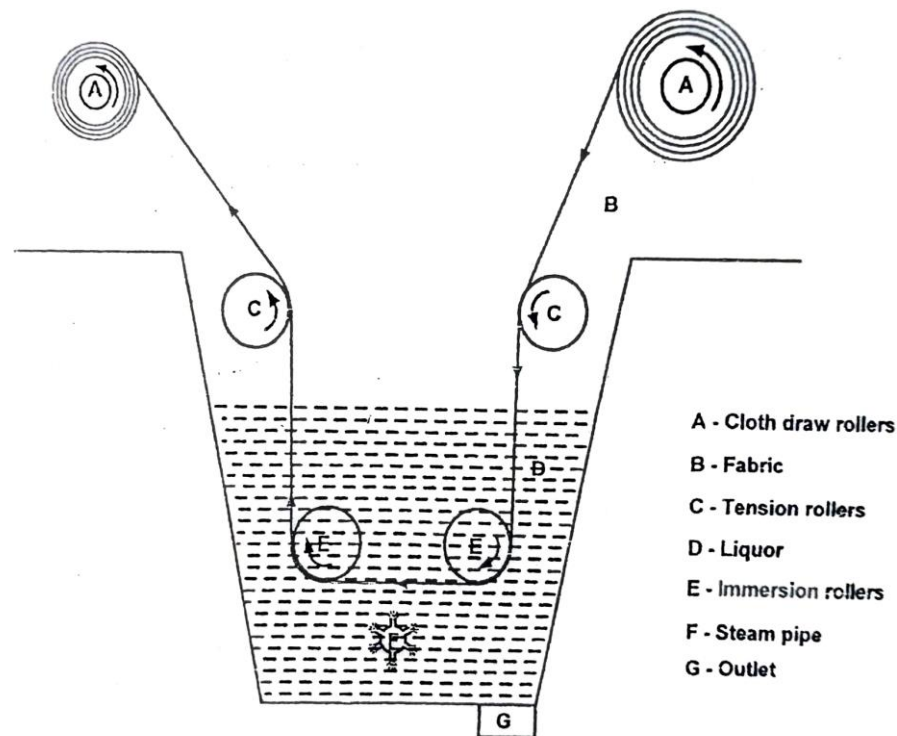F - Injection pump

Yarn package dyeing machine

I.   The machine consists of an outer vessel, mostly capable of being used under pressure, for containing the scouring, bleaching or dye liquor.

II. The yarn packages are positioned on a frame or cage provided with a number of perforated tubes in communication with a common central hollow case.

III. The wound packages of yarn are arranged one above the other on these perforated tubes so as to enclose them tightly, leaving no intermittent spaces in between packages. The cover of the outer container is then tightly secured in place.

IV. By means of a liquor pump, the liquor to be circulated (i.e., scouring, bleaching or dye liquor) is withdrawn from the outer container and forced up the tubes, outwardly through their perforations and so through the yarn packages and back into the outer liquor container. This is said to be the "inside-out" direction of flow.

V.   The direction of flow of the liquor can be reversed automatically from time to time or it may be maintained in the same direction. When it is automatically reversed, it flows 'outside-in' for a pre-set duration and then reverses in direction to flow 'inside-out' for a pre-set period of time, and then reverses again the other way and so on.

VI. The reversing mechanism is located under the main dyeing vessel and its principle of working is shown clearly in Figure.

Inside-out circulation   Outside-in circulation

1 - Liquor return flow from material   4 - Material carrier connecting piece
2 - Suction side of pump   5 - Liquor flow out to in
3 - Pressure side of pump   6 - Liquor flow in to out

The liquor reversing principle in package dyeing

VII. Package dyeing machines are normally capable of working at an M: L ratio of around 1:10.

Jigger Dyeing Machine

A - Cloth draw rollers
B - Fabric
C - Tension rollers
D - Liquor
E - Immersion rollers
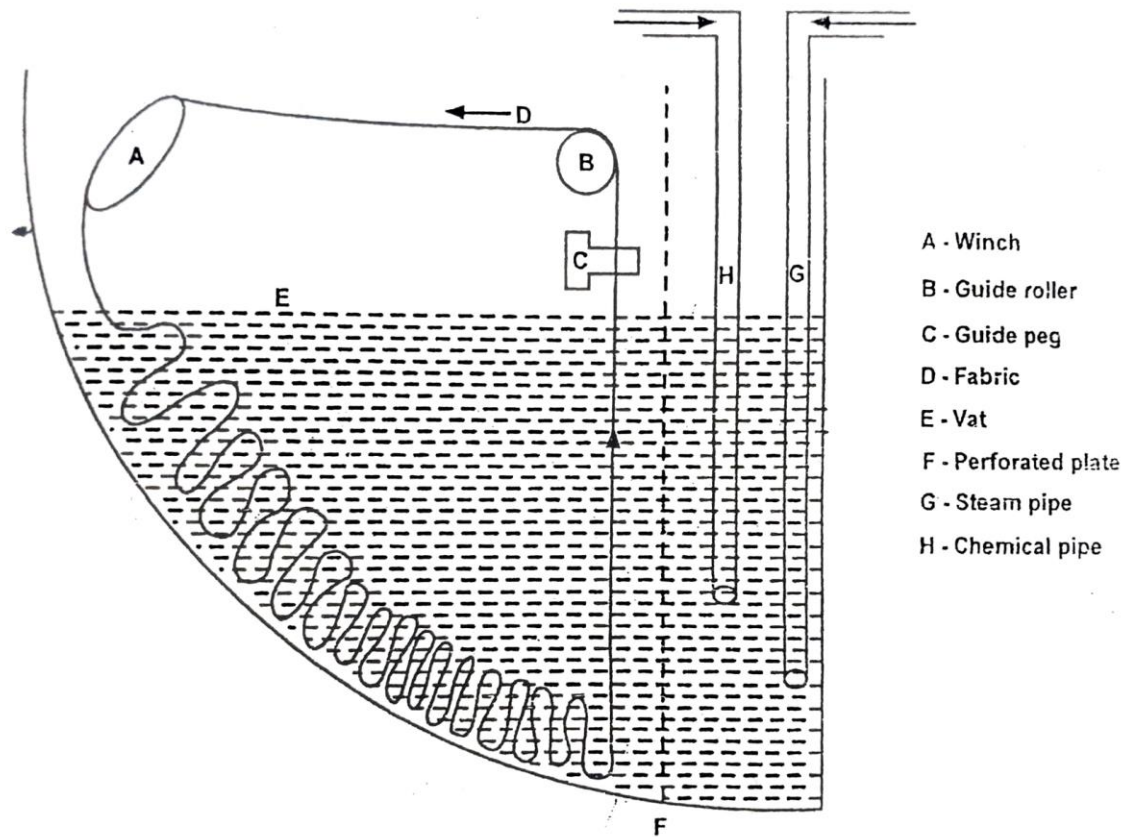F - Steam pipe
G - Outlet

Jigger dyeing machine

I.   The jigger provides a V-shaped stainless-steel vessel for containing the dye liquor, a pair of upper guide rollers, a pair of immersion rollers at the bottom of the vessel and two draw rollers to pull the fabric through the dye liquor.

II. 500 to 1000 metres of fabric, which may consist of 5 or 6 separate lengths of fabric temporarily stitched together, is wound on one of the draw rollers.

III. The V-shaped vessel in then filled with suitable dye liquor, which is then heated up to the desired temperature (depending upon the process and the type of fabric being processed) by means of a perforated steam pipe located at the bottom of the jigger.

IV. The free end of the fabric is passed downwards through the dye liquor and around the guide rollers and is then taken to the second draw roller, on to which it is tightly wound, such that the cloth in between is under tension and without creases.

V.   At this stage the second draw roller is the driven draw roller and when the machine is switched on, the fabric is drawn by it.

VI. One 'end' is said to be completed when the entire cloth roll traverses from the first draw roll through the dye liquor and then gets wound on to the second draw roll. The machine is then reversed so that the first draw roller is the driven roller and the cloth travels back through the dye liquor to be wound on to the first draw roller, to complete another 'end'.

VII. After dyeing is over, the dye liquor is run out from the vessel, which is then filled with cold water. The fabric is rinsed well in the over flowing water through as many ends as are required

to wash it free of the dyeing chemicals and wound on to a draw roller from which it can be taken away for drying or any other treatment.

VIII. It is usual for each passage of the fabric to take about 10 minutes so that dyeing takes place mostly while the fabric is saturated with the dye liquor and is on one or the other draw roller. It is usual to run the fabric at least 'six ends' in a standard dyeing cycle.

IX. The M: L. ratio in a jigger is usually about 1:5 or less.

Winch Dyeing Machine

A - Winch
B - Guide roller
C - Guide peg
D - Fabric
E - Vat
F - Perforated plate
G - Steam pipe
H - Chemical pipe

Winch dyeing machine

Construction

I. The winch dyeing machine consists of a vat (vessel) that has a curved back.
II. Over the top of the vat, extending its length is a horizontal elliptical winch rotated generally by an individual electric motor, but sometimes by means of a belt drive from an adjacent shaft.
III. Along the front of the dyeing vat is a narrow chamber, separated by a perforated plate so that the main bulk of dye liquor in the dyeing vat can pass through the perforations to mix with the bulk of the dye liquor. The steam and chemicals inlets are also located in this chamber.
IV. A fabric guide roller of small diameter extends the whole width of the vat and is positioned above the narrow chamber, but closer to the winch and at about the same height.
V. The winch is usually positioned nearer the back of the machine than the front. Textile materials are usually dyed in rope form in a winch machine.

Threading of the fabric

I. In loading a winch for a dyeing operation each length of fabric is run over the guide roll and the winch so that it falls in the vat at the rear end of the machine; the fabric is allowed to run over the rotating winch and get piled at the bottom of the machine.
II. As the bottom is sloped towards the front of the machine, the piled fabric slides along it, acquiring a wavy shape and moves slowly towards the front end of the machine.
III. When the free end of the fabric reaches the front end, it is picked up, passed between the pegs and stitched to the other free end of the fabric. Thus, the entire length of fabric is now an endless loop with much of it in a folded form at the bottom of the winch.
IV. The winch is the prime mover of the fabric, but for the greater part of the dyeing period the fabric lies wholly immersed in the dye liquor. It is only periodically that any given portion of the fabric is drawn out of the dye liquor to pass over the winch and again fall back into it. The sloped shape of the vat allows the falling fabric to slide evenly and gradually, deeper and deeper into the dye liquor.

Dyeing

I. The winch is filled with the required volume of water to give the desired material to liquor ratio, which is usually in the range 1:20 to 1:40.
II. To commence dyeing, a concentrated solution of the dyeing liquor is added to the water at the front chamber while the fabric is running. The dye liquor diffuses or passes through the perforations of the partitioning plate into the main bulk of liquor and so dyeing of the fabric commences.
III. The liquor is heated by means of the open-ended steam pipe positioned in the front chamber. From time to time additions of dye liquor and other assistants are made in the front chamber so that they mix evenly into the main dye liquor.

High Temperature High Pressure Beam Dyeing Machine
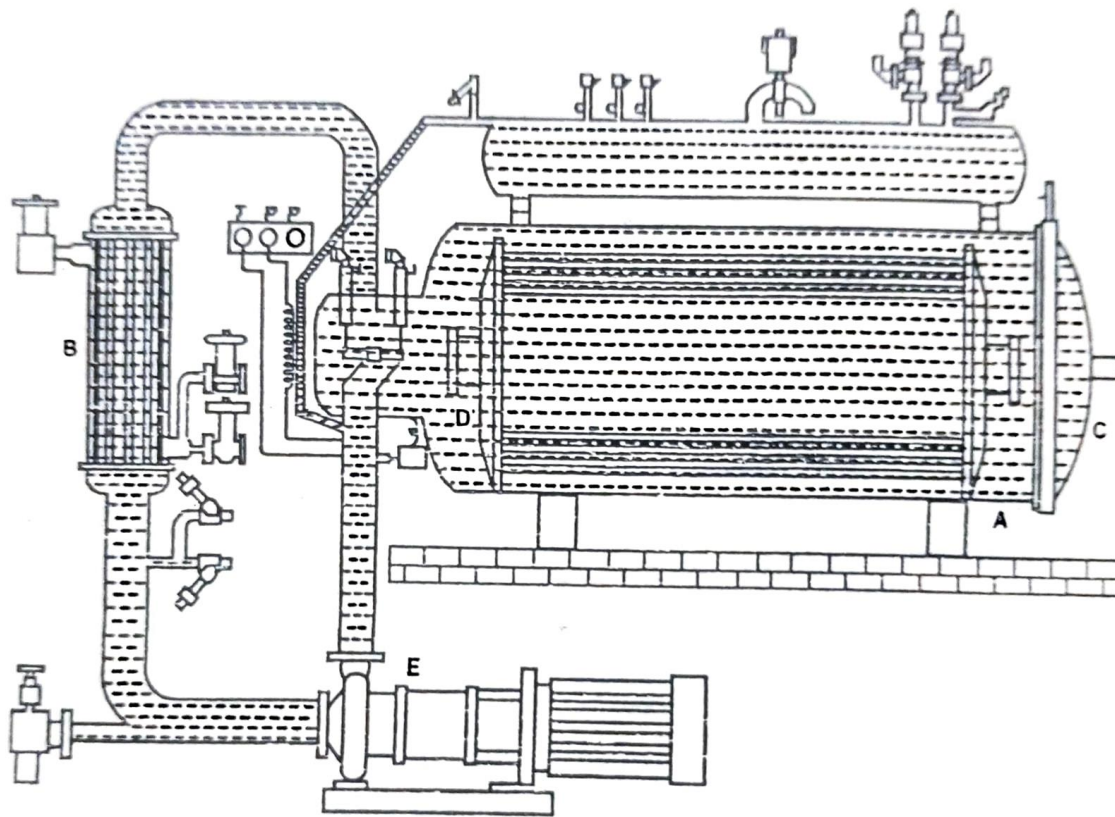
A - Main dye vessel   D - Beam with fabric
B - Heat exchanger   E - Main pump
C - Pressurised lid

High temperature beam dyeing machine

Description

I. A beam dyeing machine can dye a single large diameter beam that can be introduced into the machine's autoclave.

II. The fabric to be dyed is wound on a perforated beam which is then moved into a pressure vessel.

III. The machine is provided with a reversible flow system, i.e., inside-out and outside-in. The fabric is mostly dyed with inside out flow as with outside-in flow there is a danger of slippage of the fabric from the perforated beam; however, it may be necessary to use outside-in flow with some tightly woven fabrics.

IV. The dye liquor is forced with the help of an effective pump through the fabric wound on the beam.

V. As the dye liquor flows in a closed system, it passes through a heat exchanger by which the temperature of the liquor is automatically maintained at any desired level within a tolerance of one degree centigrade.

VI. The dye liquor is forced through the fabric at a uniform pre-ascertained pressure. The pressure and the liquor flow can be adjusted according to the nature of the fabric being dyed.

Dyeing

I. The machine is provided with a flow control valve which remains closed when the liquor circulation pump is not working. At the time of reversal of flow the valve opens slowly thereby avoiding the sudden build-up of liquor pressure which may disturb the fabric layers.

II. A special sampling device is provided to take out the sample for matching while the machine is under pressure.

Batching

I. Winding of the goods on a perforated beam is very important in the case of high temperature beam dyeing machine.

II. It is advisable to use specifically constructed batching devices, which ensure uniform batching of the fabrics with a moderate tension. Batching should not be too tight or too loose.

III. The beam is first lapped with loosely woven lapping cloth. 8 to 10 layers of such cloth are sufficient to prevent slipping of the material being dyed and avoid perforation marks. Another important factor during batching is the extent to which the material should extend beyond the perforations in the beam.

IV. Generally, the liquor will seek the path of least resistance. Hence it must be ensured that the resistance is as uniform as possible at all points on the roll of the fabric. including the edges. The overlap beyond the perforation must accordingly be more extensive.

V. A consequence of too little overlap is that there is excess flow of the dye liquor towards the outermost corner of the material and so the fabric is dyed deeper there and vice versa.

VI. To what extent the selvedges should overlap depends on the quality and density of the fabric as well as on the thickness of the roll.

Pad Dyeing Machinery or Padder or Padding Mangle

A padding machine is an open-width machine that can be used for continuous open-width or batch-wise treatment of fabric. It is mostly used for continuous processing of fabric. Very simply, a padding machine consists of a small trough to contain the padding liquor and a pair of 'bowls' or rolls to squeeze the liquor-impregnated fabric. The top roll is a soft roll (rubber covered) while the lower roll is a relatively hard one, generally of ebonite.

The function of the padder is to remove the excess liquor absorbed by the fabric in the dyeing trough by uniformly squeezing the fabric across its entire width.
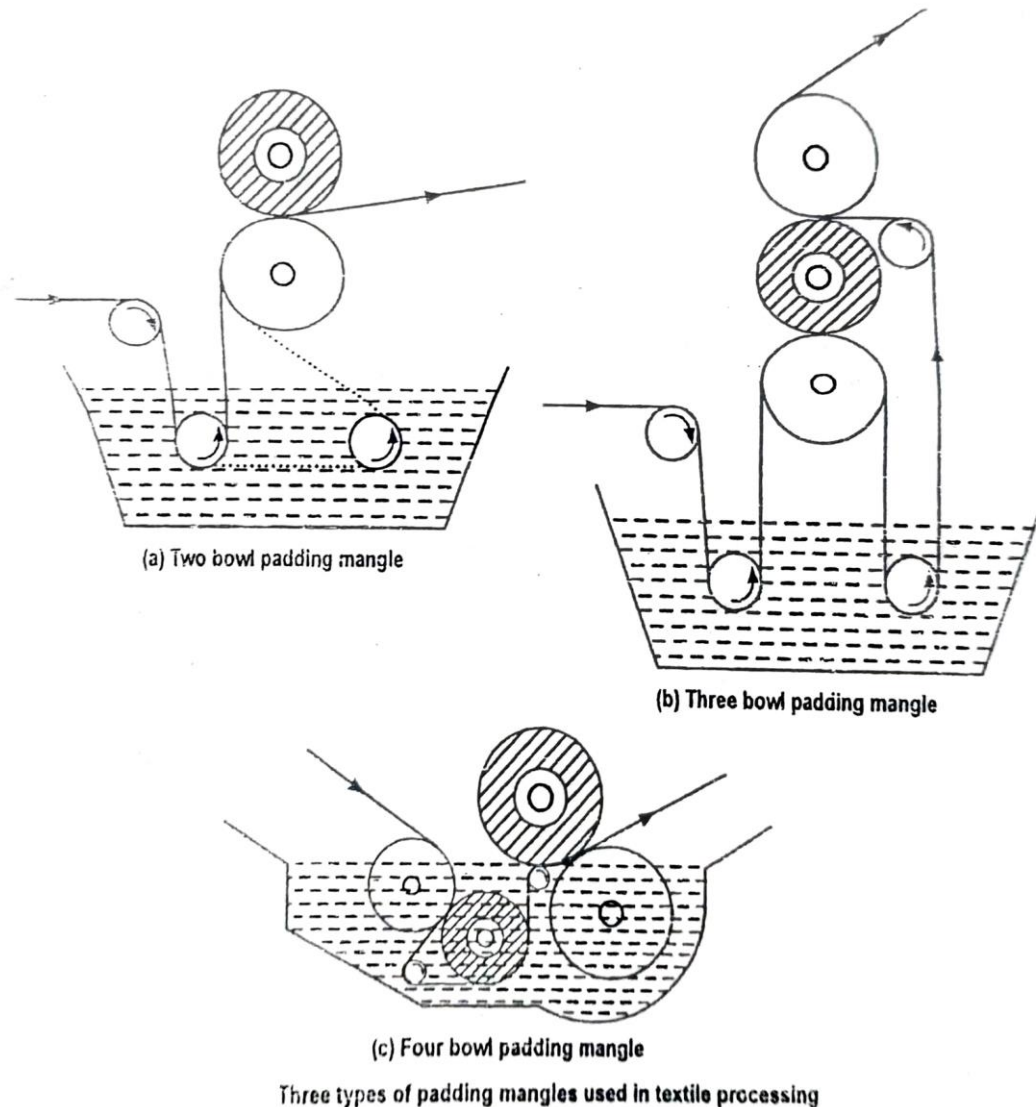
The important parts of a padding mangle are:

i) The main frames
ii) Tension elements
iii) Padding mangle bowls
iv) The dye liquor trough

The main frames are made of rigid construction to withstand heavy loads and vibrations.

The tension elements consist of a set of automatic cloth guides, to keep the fabric in a state of uniform tension without any bowing.

The padding mangle bowls: The mangle bowls are covered with rubber having surface hardness in the range 75° to 80º expressed in terms of shore hardness. There may be two, three or four bowls depending upon the necessity and the fabric being processed. The lower bowl is usually the driven roll while the other is capable of being lowered on to or raised away from the bottom bowl by means of mechanical or pneumatic pressure. When the two bowls are in close contact and the bottom roll is run, the top roll too rotates due to frictional contact. The 'expression' or pressure of contact between the two bowls can be set to any desired level within the range of the padding mangle being used.

(a) Two bowl padding mangle

(b) Three bowl padding mangle

(c) Four bowl padding mangle

Three types of padding mangles used in textile processing

The padding operation consists of the following functions:

1. **Dipping or immersing** the cloth in the liquor containing dyestuff or other treatment chemical or composition in order to facilitate the diffusion and penetration of the liquor into the material. Mainly, it helps to wet and swell the textile material and also remove air from the material.

2. **Squeezing or 'mangling'** the fabric in between the two bowls at the set pressure to compress it at the nip and force the liquor into it.

3. **Simultaneous transport of the textile material** in a forward direction. There are many types of padding mangles. A specific type is preferred depending upon the fabric to be treated and the process being used. Some examples of padding mangles are listed below and depicted in **Figure.**

a. Two bowl padding mangle

b. Three bowl padding mangle

c. Four bowl padding mangle.

Jet Dyeing Machine
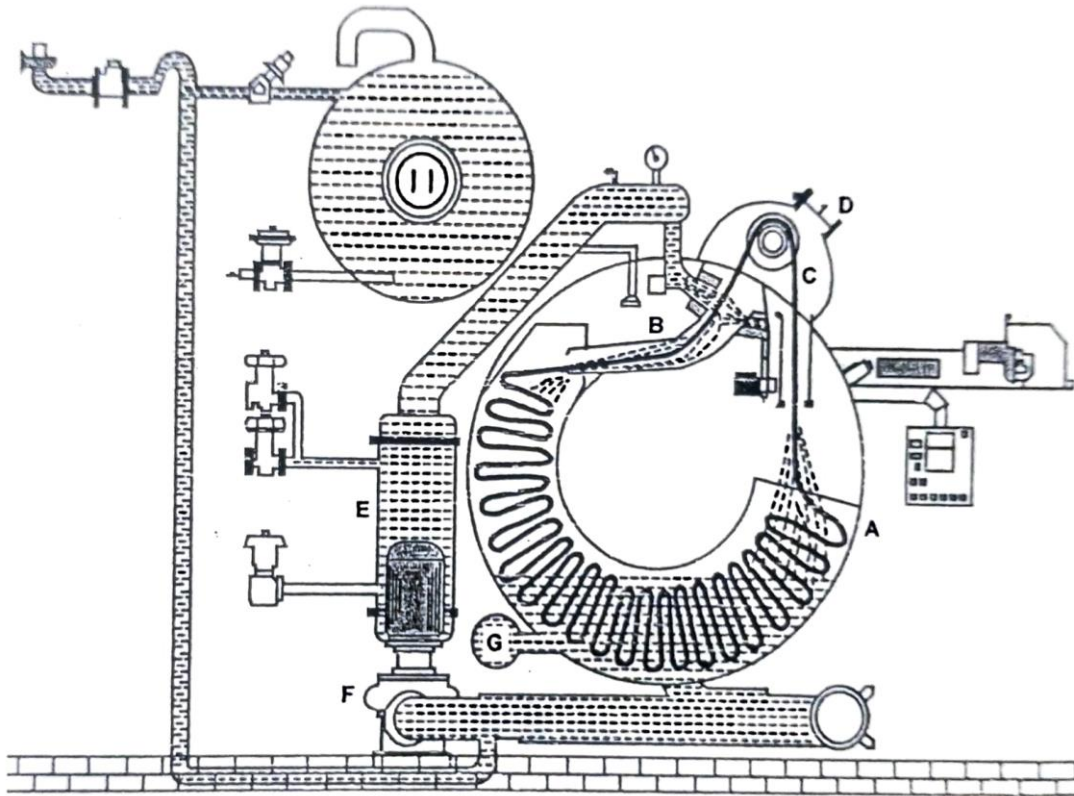
A - Main dyeing vessel   D - Slight window   F - Circulation pump

B - Jet   E - Heat exchanger   G - Dye liquor

C - Reel

Jet dyeing machine

Description

The need for more efficient and quicker methods of dyeing led to the development of the 'jet dyeing machine'. The unique feature of a jet dyeing machine is that both the fabric as well as the liquor are made to move. One of the basic principles of successful dyeing is that the fabric and the dye liquor should come into intimate contact with each other as much as possible and as rapidly as possible. This basic principle is met admirably in the jet dyeing machine.

So, the basic principle of a jet dyeing machine involves the movement of both the liquor as well as the fabric. The liquor is forced through a narrow jet or 'venturi' and this causes its velocity to increase dramatically. When fabric is also present along its path, it pulls the fabric along and transports it through the jet at great speed. Jet dyeing machines use a low liquor ratio and this aspect contributes to economising the dyeing process.

The machine consists of a main dyeing vessel, which stores the fabric and the dye liquor, a jet, a heat exchanger, a circulation pump and a cloth reel as the main parts. The continuous strands of cloth are carried in a stream of dye liquor through a cloth guide tube down into a large cloth storage chamber. Here it assumes a uniformly folded configuration and moves slowly forward through the dye bath to a position beneath a lifter reel, which presents the strand to the recirculating jet stream of dye liquor at the intake of the cloth guide tube.

The cloth is loaded by inserting the end of the cloth strand into the intake of jet where it is picked up by the jet stream and carried to the front of the cloth chamber to present itself for end-to-end sewing. Thus, the fabric is in the form of an endless loop, just as it is in a winch machine. The chief differences are that in the jet machine the liquor will also be moving, the M: L ratio is also comparatively much lower and the much higher dyeing temperatures that are possible.

The centrifugal pump circulates the dye liquor through a heat exchanger, which heats or cools the liquor as necessary without dilution. A part of the liquor is then pumped through the jet to impregnate and transport the goods being processed. The rest of the liquor flows through a bye-pass back into the beck, where it agitates the main body of the dye liquor. The number of jets determines the size of the machine and the jet used depends upon the type of fabric under process.

The capacity of the machine is about 100 - 125 kg per jet and the maximum temperature attainable is 140°C.