Subject : Dyeing And Printing

Unit 5: Dyeing process for natural fibers

Quadrant 1 – E-Text

Learning Objectives

The learning objectives of this unit are:

- Describe the dyeing process for cellulosic fibers using various dyes.

5.1 Application of Direct Dyes

Direct dyes are dyed using the exhaust dyeing method. In this method, the direct dyes are dissolved carefully, filtered and then added to the dye- bath. The cellulosic substrate is placed in the dye- bath at room temperature and dyeing is continued at this temperature for 15- 20 minutes. Then, common salt or glauber salt is added portion-wise, over a period of 45-60 minutes, while the temperature is slowly raised, to bring it to a boil.

Additions are made, by starting with a small amount of salt, followed by larger portions.
For example, the salt to be added is divided into four portions: 1/8, 1/8, 1/4, and1/2 of the total amount. The total amount of salt used, is usually in the range of 5-25%, depending on the depth of shade, liquor ratio, and the type of direct dyes that are used.
If the shade is satisfactory, the dyed material is then rinsed with cold water. At this stage, an after treatment may follow to improve the wash fastness of the dyes.

After Treatment

In a typical after-treatment, the bath is prepared with the proper amount of the cationic fixing agent, and a small amount of acetic acid (pH of bath: 5-6).

For example: 1-2% o.w.f. of the fixing agent for material dyeing with 1% of a direct dye).

The dyed material is placed in the bath, and treated at room temperature for 15-20 minutes. Then the treated material is rinsed with cold water and dried.

The light-fastness of some direct dyes can be improved by an after-treatment with copper sulfate. Small improvements of both light and wash-fastness in after-treatment, are mixtures of copper sulfate and a cationic fixing agent. Because of harmful ecological effects, many transition metal compounds, including copper compounds, are subject to effluent discharge regulations.

Striping of Direct Dyes

A complete stripping of Direct Dyes consists of two steps:

First, the dyed material is treated at the boil with a sequestering agent, such as EDTA (e.g. 1-2g. / Litre). After this, the material is treated in a second bath, with a reducing or an oxidizing agent.

5.2 Application of Reactive Dyes

Applications of reactive dyes by batch dyeing consists of three stages:

1.Exhaust dyeing 2.Fixation 3. After- scouring

Procedure

This is a typical procedure for exhaust dyeing at a high temperature. The dye bath temperature is set at 50°C and the pre-dissolved reactive dyes are added. Then the substrate is placed into the dye-bath, and the temperature is raised at 1°C per min to 80°C (about 30 min). During this time, the salt (e.g. 100% o.w.f., depending on liquor ratio and depth of shade) is added portion-wise.

Dyeing continues at 80°C for an additional 15 min., after which sodium carbonate is, added over 15 minutes. The dyeing machine is run at 80°C for 45-75 min., during which time fixation takes place. The dyed material is given two more rinses, first with warm water followed by cold water, and then dried.

5.3 Application of Vat Dyes

Vat dyes are insoluble organic compounds. They are widely used for **cellulose** fibers, and can be used for protein and nylon fibers. They produce **good color range,** but have a limited selection of orange, blue and bright green. Large amount of dyes are required for deep shades. They have excellent fastness to washing. They also have very good fastness to crocking, perspiration, chlorine bleaching, oxidizing and high temperature treatments. However, this is an expensive process, as there is high initial cost of dye and method of application.

The conventional exhaust method of vat dyes consists of four major steps: Reduction (vatting), Dyeing, Oxidation and Soaping.

Reduction (Vatting):

At this stage, the vat dye is converted into soluble form. The dye is first mixed with the proper amount of sodium hydroxide. Then, the reducing agent is added, and the temperature is raised to the recommended temperature.

The time and the amounts of reducing agent and base needed for specific dyes are shown in this Table. These are the approximate values for dyeing medium shades at a liquor ration of 1:10. The reducing agents most commonly used are Sodium Hydro Sulphite ($Na_2S_2O_4$) and Thio-Urea-Dioxide.

TYPE	IN	IW	IK
	C.I.Method 1	C.I.Method 2	C.I.Method 3
Reduction Temp	60°C	49-54°C	38-49°C
Dyeing Temp	60°C	44-49°C	21-26°C
NaOH	6-9 g/l	3-5 g/l	2.5-4 g/l
Hydrosulphite	6-9 g/l	4-6 g/l	3-4.5 g/l
Salt	None	7.5-15 g/l	10-20 g/l

Hydrosulphite get oxidized when exposed to air in the presence of moisture or in a solution. It is also very unstable at high temperatures, and therefore should be dissolved in cold water, just before adding it to the dye-bath. Thio-urea-dioxide is much more expensive than sodium hydrosulphite; however, a much smaller quantity is needed, to reduce the same amount of a vat dye. Thio-urea-dioxide is also significantly easy to handle, and more stable than sodium hydrosulphite, and is not affected by moisture.

The use of soft water throughout the dyeing process, is a must with vat dyes, since the soluble leuco salts, will form insoluble salts with calcium or magnesium ions, as well as with transition metals. Therefore, in addition to using soft water, it is common to add sequestering agents, such as EDTA to the dye bath.

Certain vat dyes may undergo over-reduction, if the reduction procedure is not followed carefully.

The factors leading to over-reduction are: Use of large amount of reducing agents. Insufficient amount of Sodium Hydroxide in the dye-bath. Dyeing at higher temperature than recommended. Therefore, in the application procedure, it is recommended to add Sodium Hydroxide, before the reducing agent.

Dyeing Procedure

The scoured material is inserted in the dye-bath and the temperature is gradually raised, to the dyeing temperature (27°C to 60°C), depending on the type of dyes used. Dyeing continues for the proper amount of time, and salt may be added to assist in exhaustion. Since atmospheric oxygen reacts with the reducing agent, as well as with the reduced vat dyes, additional amounts of the reducing agent, and the base are added during the dyeing stage. The dye-bath is checked occasionally, to ensure that the pH of the bath is sufficiently basic, (phenolphthalein paper should turn red), and that a sufficient amount of the reducing agent is present in the dye-bath (yellow vat testing should turn blue).

Oxidation

Before oxidation, the material is rinsed to remove, residues of sodium hydroxide and the reducing agent. Common Oxidizing agents used today are Hydrogen Peroxide and Sodium

Perborate. When using hydrogen peroxide, high concentrations of alkali must be avoided, to prevent damage to fibers.

Soaping

This step consists of treating the dyed material with soap at or near the boil for 10-20 minutes. Soap at the boil, increases the wash fastness of the dyes, and yields their final shade. The dyeing procedure is then completed, by rinsing with hot and cold water.

5.4 Application of Azoic / Naphthol Dyes

Naphtholation

Paste the Naphthol with Turkey red oil or sulfonated oil, and a small amount of water. Raise the temperature to 85°C. Add the required amount of alkali in the form of a concentrated solution. Continue to heat for a few minutes, while stirring.

If needed, raise the temperature to the boil, until a clear solution is obtained. The dye bath is set with water and naphthol solution, then material is entered and worked for 30 minutes. If required, salt is added during naphtholation.

After naphtholation, excess naphthol solution present in the yarn is removed. This is done by centrifuging, squeezing, vacuum extraction, or other means of hydroextraction. The purpose of this step, is to remove as much of the naphthol solution as possible, in order to avoid crocking problems.

Coupling

For the coupling to take place at a desirable rate, without affecting the stability of the naphtholate or the diazonium salt, a specific pH must be maintained for each combination used. Usually, it is in the range of pH 5-7.

Often, a mixture of Acetic acid and Sodium Acetate is added to the diazonium salt solution, to act as a buffer and maintain a pH of about 5. The naphtholated substrate is immersed in the diazonium salt solution, at room temperature for 15-20 minutes. During this time the coupling reaction would be completed.

After-Treatment

At this stage the dyed substrate undergoes a vigorous rinsing in order to:

1. Remove unreacted starting materials;

2. Remove dye attached to fibers' surface, and

3. Aggregate the dye molecules to improve wash-fastness and yield the final shade.

5.5 Application of Sulphur Dyes

The dye-bath is prepared by diluting the Soluble Sulfur Dye with the proper amount of water. A small amount of sodium polysulfide, (e.g. 1-2 % o.w.f.) and a similar amount of sequestering agent are added, and the fibers are introduced into the dye-bath at 50°C.

Sodium chloride (20-30%) o.w.f.) is added portion wise (e.g. 1/8, 1/8, 1/4, and 1/2 of the total amount) over a period of 20 minutes, while the temperature is gradually raised to the maximum dyeing temperature, usually in the range of 60-82°C.

Dyeing continues at this temperature for about 30 minutes. The material is rinsed well with warm and hot water, oxidized, rinsed, soaped at 82°C, rinsed with a mild alkali solution, and dried.

5.6 The Dyeing Process for Protein Fibers using Different Dyes

Properties	**Acid Leveling**	**Acid Milling**	**Neutral Dyeing**
Types of Acid	**Strong (2-4% H_2SO_4) (pH < 3.5)**	**Weak (2-4% CH_3COOH) (pH 3.5-5.5)**	**Ammonium Salt $(NH4)_2SO_4$ (pH 5.5-7)**
Solubility	high ---------- low		
Substantively	low ---------- high		
Level Dyeing	very good ---------- --fair		
Rate of Exhaustion	slow ---------- --fast		
Dyeing Time	relatively short ----------longer time		
Wet – Fastness	fair ---------- very good		
Colour - Range	wide range bright colours ----------moderate brightness		

5.7 Wool Dyeing

We will learn about the application of acid dyes to wool and application of reactive dyes to wool fibers.

Application of Acid Dyes to Wool

The Dyeing Procedure For Acid Levelling Dyes:

Exhaust dyeing is the method of choice for dyeing wool, and it is carried out at different stages of production: Raw stock (loose fibers), Slubbing, Yarn, or Finished garments.

This is a general Acid leveling dyeing procedure for wool:

The dye – bath is prepared at 49ºC, in addition to the acid dyes, an acid (e.g. or other acidic chemicals are added as required, to obtain the proper pH of the bath.

Sodium Sulphate (glauber salt: Na2So4, 10% o.w.f) or other dyeing assistants are added as leveling agents.

The dyeing machine is run for 5-10 minutes, after which the wetted material (raw stock, yarn, or fabric) is inserted.

The dye bath temperature is gradually raised (1º per min) to the boil, while agitating the material and / or circulating the dye solution through the material.

Dyeing is carried out for 40-60 minutes, after which the dyed material is rinsed with cold water and dried.

Dyeing Procedure For Acid Milling Dyes:

The dye–bath is prepared at 49ºC, in addition to the acid dyes, an acid (e.g. 1-3% acetic acid o.w.f) or other acidic chemicals are added as required, to obtain the proper pH of the bath.

Sodium sulfate (glauber salt: Na2SO4, 0-10% o.w.f) or other dyeing assistants are added as leveling agent

The dyeing machine is run for 5-10 minutes, after which the wetted material (raw stock, yarn, or fabric) is inserted.

The dye bath temperature is gradually raised (1º per min) to the boil while agitating the material and / or circulating the dye solution through the material.

Dyeing is carried out for 40-60 minutes, after which the dyed material is rinsed with cold water and dried.

Pre-Metallized Acid Dyes (Metal Complex Dyes)

The next step in the development of acid dyes with superior wash fastness, has been the incorporation of a transition metal ion in the dye molecule, by the dye manufacturers.

These dyes usually contain a Cr^{3+} ion (some contain a cobalt ion) bonded to one (1:1 complex) or two (2:1 complex) dye molecules by ionic and coordinate bonds.

Example of these dyes are: C.I. *Acid Blue* 158 (1:1 complex), and C.I *Acid black* 60 (2:1 complex).

The 1:1 metallized dyes are available in a wide range of colors of moderate brightness.

Advantages of 1:1 Metallized Dyes:

The 1:1 metallized dyes are easy to dissolve, and have good leveling properties.

Disadvantages of 1:1 Metallized Dye:

Their main disadvantage, however, is that they require a large amount of acid (approximately 8% H_2SO_4, pH 2) for exhaustion. This strong acidity may cause damage to the wool.

Advantages of 2:1 Metallized Dyes:

The 2:1 metallized dyes, because of their large molecular size, behave similarly to the neutral dyeing acid dyes.

The 2:1 metallized dyes are noticed for their very good wash-fastness and light fastness.

Another advantage of these dyes is that when using several different colors in the same bath, they tend to exhaust at the same rate, and to the same extent.

Disadvantages of 2:1 Metallized Dyes:

The main disadvantage of 2:1 metal dyes are, they lack bright shades, are costly, and have poor migration.

Application of 2:1 metal-complex dyes for wool fibers:

The material is pretreated for 10 minutes at 40°C in a bath containing 2-4% ammonium acetate, or ammonium sulphate, to obtain the pH range of 6-7 during dyeing.

The pre-dissolved dye solution is then added, and the temperature raised to boil in 45 minutes.

After dyeing for 30-60 minutes at boil, the material is rinsed with cold water and then dried.

Application of Chrome Dyes for wool fibers:

Chrome dyes, also called mordant dyes, are used on protein fibers where maximum wet fastness is required.

They can be applied separately with the chrome compound, and the end result of the dyeing process, is the formation of a DYE – CHROME – FIBER complex.

Chromium attached to the dye, and the fiber simultaneously, by ionic and / or coordinate bonds. The chrome compounds used are usually sodium dichromate ($Na_2Cr_2O_7$) or potassium dichromate.

Chrome Dyes can be applied by these methods: Bottom Chrome, Top Chrome and Meta Chrome.

Bottom Chrome (Chrome Mordant Method):
The chrome compound (potassium dichromate) is applied first in a separate bath, and dyeing with the chrome takes place.

Top Chrome or after chrome:

The dyes (chrome dyes) are applied first by one of the methods used for regular acid dyes. Then the chrome compound is applied, as an after treatment. The chrome compound can be applied from the same dye bath or from a new bath.

Meta Chrome:
Both the chrome compound and the chrome dyes are applied from the same bath.

Of these three methods the first two are now of historical value. The Top chrome method is being used, however, to a large extent, when dull colors with excellent wash fastness are desired.

Typical Application of Chrome Dye – Top Chrome Method

This is a typical application of chrome dye – The Top Chrome method.

The dye bath is prepared with the proper amounts of an acid, (Sulphuric acid or acetic acid) and sodium sulfate, and the chrome dyes. The fibers are introduced, and the dye bath temperature is raised to the boil in 30-45 minutes. Dyeing continues at the boil for additional 30-45 min. During this time, a small amount of acid is added if needed to complete the exhaustion.

Then the dye-bath temperature is dropped to 71ºC, by removing the part of the dye solution and replacing it by the same amount cold water.

Then the proper amount of a solution of the chrome compound is added, (e.g. for 1% Dyeing, 0.5% Sodium dichromate is used). The temperature of the bath is raised again, and kept at the boil for 30-60 min. The treatment is completed by rinsing and drying.

Advantages of Chrome Dyes

In addition to their excellent wash and crock fastness, chrome dyes have very good light fastness and very good migration properties.

Disadvantages of Chrome Dyes

The main disadvantage of the chrome dyes, is that during complexing with the chrome, a change in hue takes place. Since the color change takes place when the dye becomes firmly attached to the fiber, color matching in this method is difficult. Other disadvantages associated with the Top chrome method are, the dulling effect of the chrome on the original color, the length of time of the dyeing procedure, and the toxicity of the chrome compounds.

5.8 Application of reactive dyes to wool fibers

In a recent development, the reactive dyes offer very high degree of wet fastness. It is mainly due to covalent bonding, with wool keratin. A reactive dye also produces wide range of bright shades.

The dye bath is set with 3% ammonium acetate at 40°C to maintain a pH 7.

The material is entered, and worked in the bath for 15 minutes, and the pH is adjusted with dilute ammonia or acetic acid. After 15 minutes, 1 % dispersal (non-ionic dispersing agent) and 1% lissolamine (cationic agent) is added and the material runs for 5 minutes.

The dye solution is then added, and the temperature is raised to boil in 30 minutes. Dyeing is continued at boil for 60 minutes. The material is then rinsed and dried.

5.9 Silk Dyeing

Application of acid dyes to silk fibers

Many acid dyes have excellent affinity for silk, under neutral conditions and exhaust well at temperature below the boil.

They are the most widely used class of dyes on silk, combining brilliancy of shades, and good color fastness performance, with simplicity of application.

Boiled – off liquor is often used for dyeing. It acts as leveling agent, and keeps the silk soft and lustrous.

The dye bath is set with 100 - 500 ml per liter boiled-off liquor, and made slightly acidic with acetic or formic acid.

The material is entered at 50°C, and run for 15 minutes before adding the previously dissolved dyestuff.

The dyestuff is added portion wise, and the temperature of the dye bath is raised gradually, to 90°C. The bath is maintained at this temperature, for 30 -60 minutes until the dyeing is completed.

After dyeing, the silk is rinsed and brightened, by working in a dilute solution of acetic acid, squeezed well and dried.

In piece dyeing, 10 - 20 % glauber salt and 1- 3 % sulphuric acid, are added to the dye bath.

5.10 Application of metal-complex dyes to silk fibers

Metal complex dyes are mainly used for silk dyeing.

The dyestuff is pasted with cold water, then sufficient hot water is added and the solution is boiled to dissolve the dye completely.

The material is entered into a cold bath, containing 1-2 % leveling agent,2 - 4 % ammonium acetate or Ammonium Sulphate, or 1-2 % acetic acid (40 %) at pH 4 -5.

The dissolved dyestuff is then added, and the temperature of the bath raised to 90 - 95°C, within 30 - 45 minutes. Dyeing is continued at this temperature for 30 minutes.

Then, the material is taken out, washed, squeezed and dried.

These dyes give overall good color fastness, and also exhibit very good fastness to light in pastel shades, compared with chrome dyes.

This method of dyeing is widely used with silk in all forms.

5.11 Application of chorme / mordant dyes to silk fibers

Mordant dyes are rarely used on silk, except logwood black.

The silk is first steeped in a solution of cutch, or myrobalan extract at 50–60°C, and then steeped in a solution of pyrolignite of iron at 60 – 70°C.

It is then squeezed, and exposed to air for 1-2 hours and washed.

5.12 Application of reactive dyes to silk fibers

The reactive dyes produce bright shades, and offer good colorfastness properties, and in this respect are much superior to acid dyes. They are readily soluble in water, and possess good stability in hard water. They can be applied to both degummed and raw silk. The required quantity of dye solution is taken and 20 gms per liter, gloubers salt is added to the dye bath at room temperature (m: l ratio of 1:30).

The material is entered in the dye bath, and worked for few minutes. A further addition of 30 gms per liter glaubers salt is made, in to two portions in the next 20 minutes, and the temperature is gradually raised to 50°C. Dyeing is continued at this temperature for 30 minutes.

Further, 2 gms soda ash or 2.5 gm sodium bicarbonate is added in two portions, and dyeing further continued for 30 minutes. The material is then removed, rinsed thoroughly in cold water, squeezed and soaped for 15 minutes at 95°C in a bath containing 2 gms lisapol per liter. It is then rinsed well, squeezed and dried.

5.13 Conclusion

To summarize in this unit you have learnt the dyeing process for cellulosic fibers using various dyes.