Dyeing of Acrylic Fibres

Acrylic Fibres

- Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with an average molecular weight of ~100,000, about 1900 monomer units.
- The polymer is formed by free-radical polymerization in aqueous suspension. The fiber is produced by dissolving the polymer in a solvent such as N,N-dimethylformamide or aqueous sodium thiocyanate.
- Acrylic is lightweight, soft, and warm, with a wool-like feel. It can also be made to mimic other fibers, such as cotton, when spun on short staple equipment.

The preparation of acrylic fiber materials

- The preparation of acrylic fiber materials may involve desizing of woven materials, scouring and bleaching. Combined desizing and scouring are often possible since relatively soluble sizing materials such as modified starch.

  Polyvinyl alcohol is normally used. Scouring with weakly alkaline solutions of ammonia or sodium pyrophosphate (Na3HP207) is common.

- A non-ionic detergent is essential. Cationic auxiliary products may have substantively for the anionic groups in the fibers and block dyeing sites whereas residues of anionic product will interact with and even precipitate the cationic dyes in the bath.
  Acrylic materials sometimes have a slight yellow cast, usually a sign that drying was too severe.

- Bleaching is possible with sodium chlorite (NaClO2) and formic acid or brightening with a fluorescent whitening agent.

- Some fluorescent whitening agents can be used in the presence of sodium chlorite, allowing combination of the two methods.

- Stabilizers that control chlorine dioxide emission such as borax or polyphosphates should be used. A corrosion inhibitor such as sodium nitrate is essential when using steel equipment.

- Some cationic dyes are very sensitive to traces of chlorine and will rapidly fade giving poor colour yields, particularly when dyeing pale shades. An anti-chlor treatment of fabric bleached with sodium chlorite may be necessary and small additions of sodium bisulphate or thiosulphate to the dyebath will avoid problems with cationic dyes sensitive to traces of chlorine in municipal water.

Dyebath preparation

- The dye powder is usually made into a pastedwith acetic acid and then mixed with boiling water. Cationic dyes with delocalized cationic charges are intensely coloured and it is essential to avoid dust escaping from the powders.

- Concentrated liquid dyes do not have this problem. Solid forms of these dyes are often not easy to dissolve because of their tendency to form gummy material. Preparation of a paste with methanol and addition of warm or hot water is sometimes a useful alternative.

- Some cationic dyes are not stable in boiling water. Many react with alkali to give colorless products such as the free amine from neutralization of an ammonium ion group, or a carbine by reaction of the cationic group with hydroxide ion.Dyeing with cationic dyes therefore invariably takes place in weakly acidic solution to avoid these problems.

Dyeing of Acrylic fibers

- They have some undesirable properties in respect of dyeing –
  - Poor solubility in industrial solvents
  - High melting point making hot drawing difficult
  - Low saturation absorption of dyes

- Dyeing Properties can be improved by using Co-Monomers e.g. Vinyl acetate, Acrylic acid etc.

- These groups introduce weakly acidic groups .

- Method of spinning which introduces voids also affects dyeing of acrylic fibers.

- Cationic dyeable acrylic fibers are most important types of acrylic fibers to be dyed.

Dyeing procedure

- Acrylic fibers may contain a variety of different anionic groups. These include a limited number of terminal sulphate and sulphonate groups arising from the persulphate polymerization initiator .

- In other types there may be appreciable numbers of carboxylate groups from acrylic acid or similar monomers added to the acrylonitrile before polymerization. These anionic groups are responsible for the substantively of cationic dyes for such fibers. Comparison of equilibrium dye adsorption as a function of pH when Dyeing acrylic fibres are dyed with cationic dyes.

The actual process

- The dye solution is often prepared by pasting with acetic acid, and a stable pH at 4.5 5.5 can be obtained by addition of sodium acetate to buffer the solution. Dyeing at around pH 5 suppressed the dissociation of any carboxylic acid groups in the fibre and thus controls the dyeing rate. An increased dye uptake of the acrylic fibre with carboxylic acid groups (b) as the acid groups dissociate and become anionic above pH 6.

- The number of carboxylare groups in an acrylic fibre varies from one type to the next. Level dyeing requires strict control of the pof cationic retarding agents. The latter initially block the anionic sites in the fibre and are gradually replaced by the more. An addition of up to 2.5 g 1-1 of anhydrous sodium sulphate helps to offset the negative surface charge and sodium ions weakly block anionic sites in the fibre. Both effects decrease the initial rate of dye absorption.

- Sodium sulphate is not as effective as cationic retarding agents that have some substantively for the fiber. shows a typical dyeing procedure.

- After dyeing is complete, the bath is slowly cooled to 50-60 C to avoid these problems. Rapid cooling by addition of cold water to the dyebath cab can be disastrous as it causes immediate setting of creases in the goods. The material is finally rinsed and possibly given a mild scour with a non-ionic detergent and a little acetic acid plus a softening agent.

Mechanism of Dyeing

- It consists of three steps ---
  - Colored cations of ionized dye are absorbed on acrylic fiber surface.
  - Absorbed dye cation diffuse in the interior of fiber at particular temperature.
  - Cations are attracted and retained by anionic sites in the fiber substance by strong electrostatic attraction forces.
  - These steps gave fabric good washing fastness.

Process of Dyeing

- Two ways of obtaining perfectly even distribution to dyestuff in acrylic fiber ---
  - Migration properties of the dyestuff can be utilized to get desired effect, provided the dyestuff is not immediately fixed during adsorption on fiber surface and fiber sites having affinity for dye stuffs are distributed evenly in fiber.
  - The build up of dyestuff during first phase of dyeing can be controlled so that no migration takes place after absorption.

Dye Class

- The dyes used for acrylic fibers are –

- Disperse Dyes
  - Low affinity
  - Suitable only for pale to medium shades

- Cationic or basic dyes
  - Most suitable dye class
  - Can produce deep shades with good fastness properties
  - Widely used

Regulation of Dyeing Process

- It can be done by –
  - Adding cationic or an anionic product to the dye bath.
  - The dye cations absorbed initially on the fibre surface resist diffusion into the interior of the fibre. Any significant diffusion is possible only by the freeing of the dye molecules from their local interactions with the polymer. This is effected by elevating the temperature of the dyebath. This temperature increase make motions of the obstructing polymer chains also become greater or easier. These two distinct effects of temperature combine to assist the penetration of the dye into the fibre.
  - If the dye initially exhausts unevenly, it is then very difficult to level the dye, so it is extremely important to control the initial rate of strike. This initial rate of strike is controlled by use of retarding agents.

Retarding Effect

- To solve problem of even dyeing on acrylic fibres various approaches have been developed including the use of temperature as well as cationic and anionic retarders.

- There are two types of retarding agents --
  - (a) those that form a complex with the dye and thus tend to retain it in the dye bath
  - (b) those that compete with the dye for the ionic dye sites in the ion exchange dyeing process.

Retarder

- The ideal retarder for acrylic should –
  - Provide level, uniform dyeing.
  - Allow full saturation of dyeing
  - Permit full bulking of bi-component fibers
  - Be usable with softeners
  - Show overall exhaust rate sufficiently.

- A cationic retarder based on a quaternary ammonium compound competes with the cationic dye for the anionic dye sites in the fiber. This competition reduces the initial strike rate of the dye, to promote level dyeing, but may also reduce the final dyebath exhaustion.

Effect of temperature on dyeing of acrylic fibers

- Above the dyeing transition temperature (TD) under the actual dyeing conditions, cationic dyes tend to exhaust very rapidly over a small range in temperature.
- Great care is needed at temperatures just above TD to avoid unlevel dyeing.
- The rate of diffusion of the cationic dyes into the acrylic fibre is very slow below TD because of the absence of the required polymer chain mobility. The rate of dyeing increases rapidly above TD.
- Once the acrylic fibre becomes accessible very careful temperature control is required. For this reason, once the bath tempetature reaches 70-75 C, the rate of heating Is usually significantly decreased.
- The careful temperature control required when dyeing acrylic fibres with cationic dyes is necessary to avoid unlevel dyeings.

Properties of Cationic Dyes

- Compatibility
  - The behavior of dyes in admixture is of great practical interest. Level and repeatable dyeing are achieved more easily if dyes of almost equal behavior in admixture can be selected.
  - Compatibility of cationic dyes can be defined in level dyeing ratings after assessing the dyeing from 5-1 also known as Compatibility Value.
  - This can be understand by example – A dye with a compatibility value five is more leveling since it is adsorbed more gradually than a dye with compatibility value of 1.

Propertries (contd.)

- Saturation Value
  - Depending on the composition of fiber, degree of draw, percent crystallinity etc. acrylic fibers differ in the rate of dyeing with cationic dyes.
  - A saturation values has been assigned to this rate of dyeing which is 2.1% for shades obtained by mixing green crystals of Malachite green.

Properties (contd.)

- Saturation Limit
  - Each cationic dye has a saturation limit on a given acrylic fiber at which it reaches a max. depth.
  - This limit depends both on type of fibre and dyestuff.
  - Determined experimentally by dyeing in absence of any retarder.
- Saturation Factor
  - Ratio of saturation value (2.1) and saturation limit.
  - It is a characteristics property of cationic dye.

Defitherm Process

- A standard process of dyeing acrylic fibers with cationic dyes as proposed by BASF on the basis of fiber and dyestuff.
- In the process bath being exhausted at a constant temperature, concentration differences being avoid by adding dye in concentrated form.
- Quaternary ammonium compound Defithermol TR is used, which is a thermoregulator as well as retarder.
- In calculation defitherm values the % of the dye is expressed as Defithermol TR.