drug there is the danger of resistant strain being developed, with the other there is the inconvenience of gulping large oral doses or of its being costly and out of reach of the poor sufferer. It is to be hoped that the intensive work going on in the various parts of the world, may soon evolve an ideal drug to eradicate tuberculosis, the Public Enemy Number One !

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Recent Developments in the Dyeing Technique

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IN recent years considerable amount of literature has been published on the subject of dyeing with vat colours. The application of vat colours to cellulosic fibres in package form as well as to fabrics by continuous methods and to wool and other synthetic fibres has called for many improvements in the usual methods of dyeing. Continuous method of dyeing which is being widely employed in modern times, yields not only greater production at low cost in the shortest possible time, but also ensures minimum damage to the material as the period of contact with the various chemicals is short. Temperature plays an important part in the rate of dye absorption and in the degree of penetration—they being increased with increase in temperature. This fact is made use of in the modern continuous dyeing methods. However, it has been the experience in the vat colour dyeing that the rate of exhaustion of the dye-bath is much higher than the rate of penetration into the interior of the fibre. This lack of balance causes uneven surface dyeing, particularly while dyeing in package form. In order to equalise these two rates of absorption and penetration in the process of dyeing, starting the dyeing at low temperatures and slowly raising the temperature of the dye-bath is practised as the rate of absorption is practically negligible at low temperatures. There have been many improvements[1] in this direction. The first is the use of retarding agents which lower down the rate of exhaustion. Such retarding agents are glue, sulphite liquor, paragol O, albetex P.O., dispersol V.L., etc. Another suggestion made to balance the rates of dye absorption and penetration is the addition of certain solvents to the dye-bath, such as methylated spirit, carbitol, butyl-carbitol, etc. which increase the rate of penetration by forming nearly molecular solutions of the dye. However, the high cost of these solvents prevents their commercial application. Yet another method for satisfactory dyeing makes use of the poor affinity of the acid-leuco-compound of the vat dye, unlike the sodium salt which exhibits

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great affinity to the fibre. The vat colour which has been dissolved in caustic soda and hydrosulphite is brought to pH 4.5—5.5 by adding acetic acid, and the precipitated leucovatacid dispersed in a dispersing agent and the dyeing started with such dispersions. After allowing some time for penetration the dyeing is completed in the solution of the sodium salt by adding alkali and hydrosulphite. The last and the most important of these improvements is the treatment of the material prior to dyeing in the fine dispersions of the dye pigments. In the Abbott Cox process the vat dye in its unreduced form is dispersed in Dispersol V.L. (0.5 to 1.0% solution). Finer the particle size of the dye, better the dispersion and consequently quicker the penetration. Hence for obtaining finely divided dye particles grinding in homogenisers or still better in ball or pebble mills for long periods is done. In fabric dyeing the penetration of the pigment into the interiors of the material can be quickly achieved by mechanically forcing it up by the pressure in the nips of the pad rollers. As a preliminary step for the continuous dyeing of fabrics the question of the rate of penetration is successfully solved by this pigment padding process.

Continuous dyeing is not a new process, but the old methods were not economical nor were the dyeings uniform. Whereas the wastage incurred when the dye-baths containing dyes and chemicals are thrown down at the end of dyeing may not be considerable while handling very large yardage of cloth, a successful process should prove economical even with small lots of cloth. The conditions to be fulfilled for such a process would include the ease of changing from one shade to another, quickness in attaining the absorption equilibrium, minimum waste of dyes and chemicals left behind in the bath and resulting in uniform and good penetration. Some of the recent developments in this field will be described briefly here.

I. *Pad Steam Process :—*

This was developed in Germany and later adopted by Du-Ponts in America. The cloth is pigment-padded, dried in hot flue, cooled to minimise bleeding and again padded below 40°C in a solution of caustic soda and hydrosulphite along with salt and some rongolite to minimise bleeding. It is then entered into a steaming chamber where it is subjected to a saturated steam atmosphere slightly above 100°C with complete exclusion of air. Reduction and fixation of the dye is completed in 10-20 seconds. The cloth then is further carried in open soaper range for oxidation, soaping, etc.

The wastage of chemicals is minimum as the cloth is run in the short liquors contained in padding mangles. The working speed is about 100-120 yds. per minute and the minimum practical run is about 5000 yds. Well penetrated uniform shades are obtained in this process. The fabrics worked on this machine are cotton, rayon and at times nylon ; vat, sulphur and direct colours are applied.

II. *The William's Unit and the Hot Oil Dyeing Process*[2]*:—*

The William's Unit was constructed to minimise wastage incurred by the large volumes of the liquor required to be thrown from the usual booster boxes. The unit consists of narrow boxes with a roller each at the top and bottom and with baffles and heaters in between. The movement of dye liquor by the baffles leads to improved penetration. The dyeings carried out near 100°C yield satisfactory results by rapid reduction and fixation of the dye.

An important advancement made by the inventor of the William's Unit is the use, in the same unit, of hot mineral oil which supplies the necessary heat for the fixation of the dye and at the same time causes no bleeding. The caustic hydrosulphite padded cloth is passed into the hot oil-bath at 100-120°C in accordance with the type of the vat dye and the reduction and fixation completed in about 30 seconds. When the wet cloth comes in contact with oil well above the boiling point of water violent reaction takes place—the water vapour forming a steam-in-oil emulsion. Some modifications to the unit have been made in order to provide enough space for the increased volume of emulsion by lowering down the rollers and the baffles in the narrow box. Air should be prevented from entering oil-bath during the dyeing operation. After the passage in the oil-bath the cloth is passed in a booster box through a stream of cold water containing a good emulsifying agent such as Igepal C.A. to remove the adhering oil. Then follow oxidation and soaping during which some quantity of emulsifying agent is added to free the cloth from oil as much as possible.

The chief advantage claimed by this method is the easy adaptability of the old units already installed in the mills. Speeds up to 150 yds. per minute have been satisfactorily used. Minimum yardage is 1500 yards or more. Fixation by this process is quite good ; however, good levelness can be obtained only by an aqueous developing bath. The method is applicable to cellulosic fibres.

III. *The Standfast Molten Metal Process*[3]:—

The credit of employing molten metal as the heat-treating medium goes to the English authors, Hannay and Kilby. The fusible metal employed is an alloy containing 50% bismuth, 25% lead, 12½% cadmium and 12½% tin melting at about 65°C and having a molten density of about 10. The machine is extremely simple in operation. It consists of an iron vessel in the form of a large U of metal 5 ft. wide, 5 ft. deep and 1 inch thick. The cloth is passed down one arm and up the other via a guide roller at the bottom. Steam heating pipes are arranged on both sides of cloth to maintain an even temperature of the molten metal. On the entry side there is a stainless steel bottomless dye-bath, the molten metal acting as the resting surface for the dye liquor. At the exit end there is a similar box containing salt solution as the waste liquor. The preheated cloth is first saturated with the dye solution. It then enters the molten metal maintained at 95-105°C and gets squeezed by the pressure in molten metal. The colour fixation is effected during the passage. The cloth is washed in the salt solution at the exit end and then passed in the usual range for rinsing, oxidation, soaping, etc.

The outstanding qualities of the moltem metal process are: (1) its ability to exert uniform squeezing effect in accordance to the thick and thin portion of the fabric, (2) complete exclusion of air during the passage resulting in saving of caustic and hydrosulphite, (3) its suitability in handling small yardages. The squeezing expression is about 140% thus allowing to carry through more dye and chemicals. The cleaning time necessary for changing shades is very short as the machine is extremely simple—shade variation (end to end and side to side) is nil. Shade matching is easy as the laboratory model of the machine can predict the conditions for the bulk machine. The speed of operation varies from 30 to 120 yds. per minute ; the minimum yardage is less than 500 yds. The penetration is not found to be good but it can be improved by pre-padding the cloth in the dispersed pigment. The work done so far on this machine is the dyeing of cellulosic fibres with vat dyes. Sulphur colour cannot be worked as the formation of cadmium sulphide will cause trouble. The loss of metal during long runs has not been found to be much, provided care is taken not to use chemicals that would react with the metal.

IV. *The Bond Machine*[4]:—

The bond machine manufactured by the Hussong-Walker Davis Co. in the U.S.A. is a recent improved continuous dyeing machine suitable for dyeing with almost all classes of dyes over a wide range of textile fibres—cotton, rayon acetate, nylon, orlon, dacron, wool, etc. The principle of the ordinary bath-room shower nozzle has been adopted in this machine to give quick penetration. The cloth is passed between two perforated metal plates through which the hot dye liquor is forced into the fabric, the dye liquor forming a continuous sheath on both sides of the fabric. Good penetration is effected by the pressure with which the liquor is forced through the nozzles. Dyeing is completed in a very short time. Any pile fabric can be dyed uniformly without distortion in this machine. Speeds from 20-120 yds. can be used and very small yardages can be run economically.

V. *The Vat Craft Process*[5]:—

This process, developed some years back by the Vat Craft Corporation is based on the application of atomic energy to vat colour dyeing, but full details of the process and its working are not available. It consists essentially in coating the fabric with soluble materials, which on exposure to radiation are converted into insoluble coloured pigments, a radio-active catalyst U.A.1 being used for the same. The cloth padded in the dye solution containing the small quantity of the radio-active material U.A.1 is passed through another bath containing photosensitizing material and it is then exposed to the most concentrated light radiation in the development chamber when conversion into insoluble coloured pigments takes place and the colour gets fixed into the fabric. The fabric leaving the chamber is rinsed in a fresh water-bath and is ready for final finishing operations. The speed is about 125 yds. per minute and minimum yardage about 5000 yds. The cost of dyeing by the vat craft process is claimed to be comparable with other vat dyeing processes.

Printing with vat pigments by employing resins in the paste is quite well-known. Similar surface dyeing with vat pigments to get fast shades is described in one of the recent patents. The cloth is padded in a caustic soda solution of cellulose ether which has been pre-dyed with the vat colour and then fixed up by passing it in an acid solution.

With the advent of the new synthetic fibres which are generally hydrophobic, the application of the common classes of water-soluble dyes to these fibres had been a great problem to the dyers. It is now established that at elevated temperatures above 100°C all these fibres swell sufficiently and could be dyed to deep shades. High temperature dyeing above 100°C is found to be more advantageous even with ordinary fibres, particularly with wool, as it saves considerable amount of dyeing time. Some machines recently developed for dyeing at elevated temperatures will be described below.

(A) Autoclave type machines for dyeing in batches.

(i) *Rotary dyeing machine specially suitable for synthetic fibre knitwear*[6]:— The machine has an internal rotating perforated cylinder with four separate compartments so as to maintain the knitwear goods evenly spaced during dyeing. It is encased in a strong vessel which can be closed air-tight to develop pressure. The inner cylinder is rotated at the rate of about six revolutions per minute with reversal of the direction of rotation every half minute. The temperature of the liquor is raised above boil by closed steam coils.

(ii) *Steverlynck system of package dyeing, suitable for fibre and yarn*[7]:— This machine overcomes the difficulties met in the pressure dyeing process viz., (1) addition of dyes and chemicals during the course of dyeing, (2) the removal of samples to follow the course of dyeing without loss of pressure and (3) efficient running of the pump even when part of the liquor is transformed into vapour. By filling the dye vessel completely with the dye liquor and providing a small expansion chamber which is in communication with this vessel through a valve, the troubles associated with the pump are avoided. During dyeing the valve is kept open and the expansion chamber filled with compressed air. It is through this expansion chamber that additions of dyes and chemicals and removal of samples are effected without loss of pressure.

(iii) *Barotor*[8]:—This machine, produced by Du Gonts is useful for dyeing of piece-goods at high temperature and pressure. It consists of a horizontal autoclave with an inside rotor which could be loaded with about 600 yds. of cloth in single layers. By an ingenious device the cloth itself is made to move forward relative to the rotor, so that even with the smallest quantities of the dye liquor every portion of the fabric has equal accessibility. A special arrangement consisting of a pipe connected with the vessel through two gate valves enables the drawing of samples and making additions to the dye bath without loss of pressure.

(B) Continuous machines suitable for elevated temperatures:

(i) *Thermosol process*[9]:—This method developed by Du-Ponts is applicable only for Dacron Polyester fibres and is based on the principle that when fabric coated on the surface with the dye is subjected to temperatures of the order of 350 to 400°F the dye penetrates into the interiors of the fibre and gets fixed. The fabric is coated with the dye from an aqueous dispersion in a padding mangle, dried thoroughly in a hot flue and then cured in the thermosol unit at the high temperature for a period of less than two minutes. Scouring, soaping, etc. follow in the usual manner. Speed is about 15 to 40 yds. per minute. Specially selected acetate dyes and some vat dyes are used in dyeing on Dacron.

(ii) *Uxbridge machine*[10]:—The Uxbridge developed by Beckman Uxbridge Worsted Corporation is the latest continuous dyeing machine suitable for dyeing at elevated temperatures. The machine is so constructed that fabric is continuously fed in and drawn out of the pressure chamber without loss of pressure. This is made possible by a set of three sealing rollers which seal the mouth of the chamber and at the same time rotate and lead the cloth in and out. The padded cloth enters chamber through the sealing rollers and is carried over guide rollers working in a tank containing the dye liquor or the developing liquor. Speed, temperature, pressure, immersion time, volume level and pH of the liquor—all can be controlled.

The machine is suitable for dyeing almost all classes of fibres, both natural and synthetic with the only exception of Dynel which does not withstand high temperature. Selected dyes belonging to all classes can be applied. The working speed is about 30 yds. per minute and the minimum run about 2000-5000 yds. The temperature is varied from 270 to 300°F, the fixation being effected in 12-60 seconds depending on the type of the fibre and the dye. Excellent penetration and good levelness are claimed by the process.

Before closing this article mention has to be made of some recent application of sonic and ultrasonic vibrations in the field of dyeing.

Ultrasonic waves are compressional waves, similar to sound waves, but having frequencies too high to affect the human ear i.e. about 20,000 cycles/sec. These would be produced by exciting certain piezo-electric crystals, like quartz, into rhythmic oscillation by applying an alternating electric potential. However, this method could not be used on a large scale for industrial purposes, owing to the nonsuitability of the small crystals. A new ceramic crystal[11] from barium titanate which could be made to any size and shape has overcome these difficulties. When dye liquor is subjected to ultrasonic vibrations the forces of acceleration and cavitation act upon the water, the dye particles and the fibres—and thus cause deæration of dye liquor and goods, better dispersion of the dyestuff and loosening up of the fibre structure. All these assist a rapid establishment of equilibrium.

Brauer[12] has made experiments on dyeing with vat colours using sonic and ultrasonic vibrations ranging from 50 to 175000 c.p.s. and has made the following observations:—

(1) Even the sonic waves give deeper shades than those produced under similar conditions by normal dyeing. (2) Ultrasonic waves have proved to be more efficient than the sonic waves in establishing the equilibrium. Thus the time in dyeing can be reduced to 1/4 to 1/6 of the normal dyeing time. (3) There is perfect dye penetration even in closely woven fabrics. However, caution has to be exercised in the use of these vibrations as they are likely to damage the fibre structure.

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