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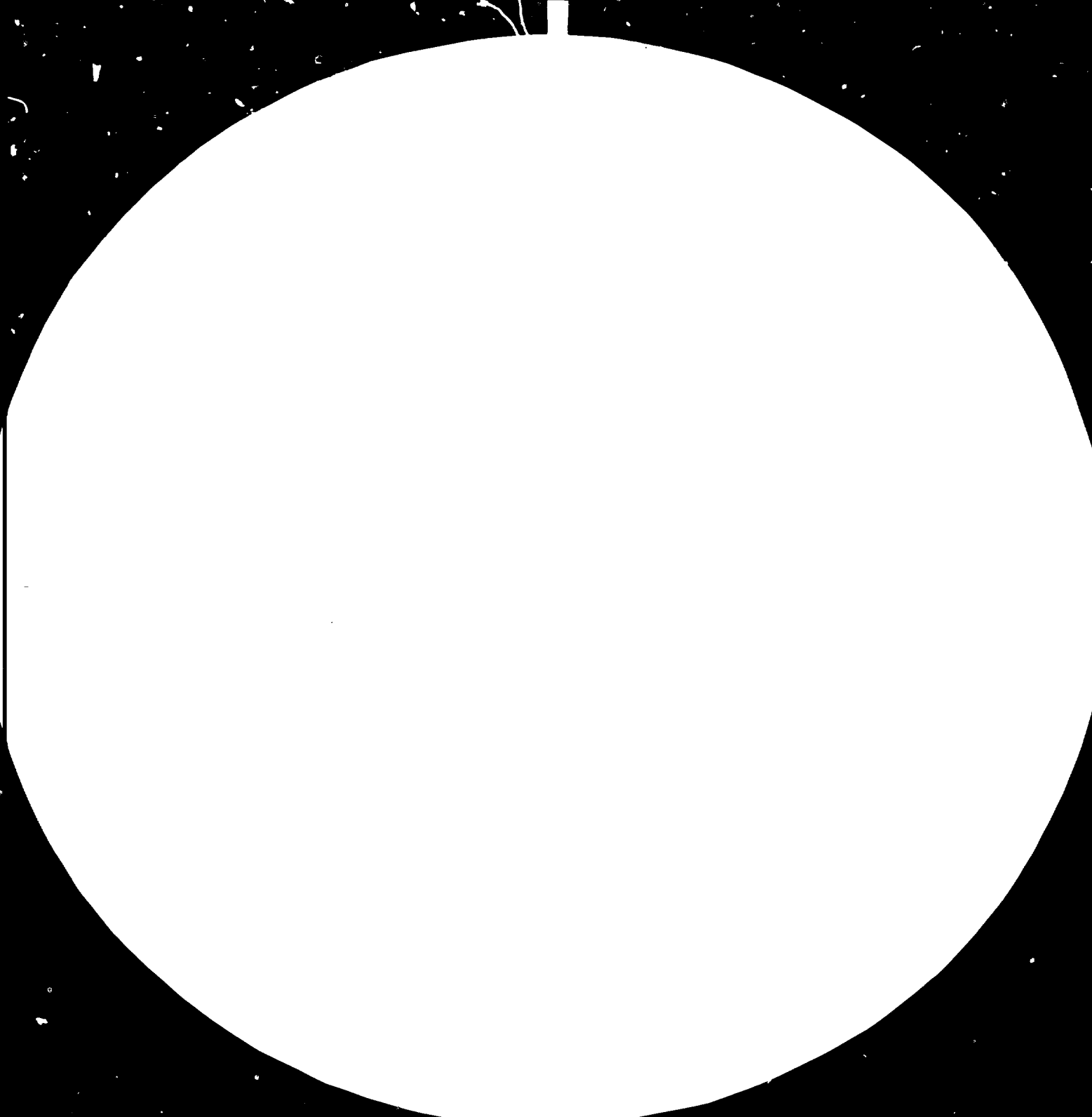
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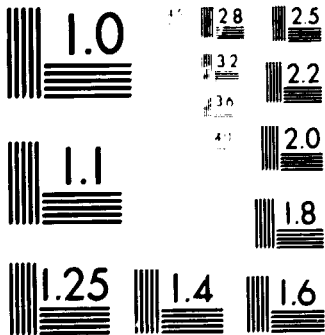
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DYEING OF SYNTHETIC FIBERS AND BLENDS

Dr. Walter Lebersaft

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DYEING OF SYNTHETIC FIBERS AND BIENDS

Dr. Walter Lebensaft

Introduction

With the dyeing process which is normally carried out from aqueous solutions, the dye from the dyebath becomes concentrated in the substance of the material being dyed. This involves

- 1) the transport of dye through the dyebath to the fiber surface,
- 2) the adsorption of dye at the fiber surface,
- 3) diffusion and adsorption of dye within the fiber.

In principle, any one of these steps may control or influence the rate of dyeing. The more efficient the agitation of the dyebath, the less important is step 1. Step 2 can be important when the transfer of dye from the bulk phase to the fiber surface is influenced by a barrier. Such barriers might arise from electrical interactions between dye-ion and fiber or from the morphology of the fiber. The rate of dyeing is most likely influenced by step 3. The diffusion and adsorption of dye within the fiber is not only dependent upon the chemical nature of the fiber but also by the resistance that the polymer structure imposes on the movement of dye.

The forces of adsorption are due to interactions which occur between polar and polarizable molecules. Because of adsorption a fraction of the total amount of dye present in the fiber is immobilized and not free to diffuse. Consequently, the diffusion is dependent on the equilibrium between the concentrations of free and adsorbed dye in the fiber.

The resistance to dye diffusion by the polymer structure is related to the molecular order and morphology of the fiber. Thus, mechanical treatments, e.g. stretching or drawing of nylon filaments, which cause changes in density and orientation, result in a decrease in rate of dyeing. When polyester is heat-set the crystallinity of the fiber and the glass transition temperature are changed. This causes a decrease in the rate of dye penetration.

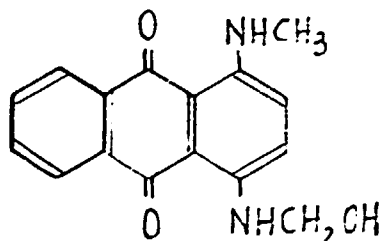
When processing has been carried out under conditions which have been non uniform, the variations in the structural effects produced, will show up as unlevel dyeing properties.

Dyeing of Polyamides

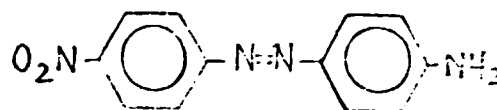
Polyamides do have ionic groups (end groups) in the polymer structure and therefore can be dyed by ionic dyes, such as acid- and premetalized dyes. On the other hand polyamides exhibit low swelling in water as compared to natural fibers. As a consequence they provide a good environment for the non-ionic disperse dyes. Another possibility is the use of reactive dyes which form a covalent bond with the fiber molecule.

1) Disperse Dyes (non-ionic dyes)

These dyes were the first to be recommended for dyeing polyamides, e.g.



C.I. Disperse Blue 3



C.I. Disperse Orange 3

Disperse dyes exhibit a very low solubility in water. Therefore they are produced in a form which will readily disperse in the dyebath. The significant feature is that they have a high solubility in polyamide. During the dyeing process the low concentration of dye dissolved in water is extracted by the stronger solvent, the polyamide. The equilibrium sorption of dye by the fiber is directly proportional to the concentration of dye in the dyebath, up to a definitive limiting sorption or "saturation" value. This yields linear sorption isotherms (fig.1).

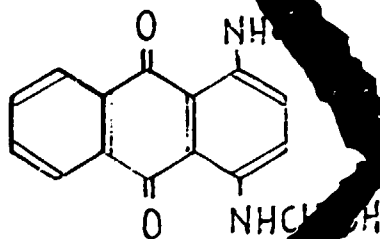
Since the dyes are held only by relatively weak solute-solvent forces, they are mobile and provide optimum levelness. There is also a lack of any interactions between

Dyeing of Polyamides

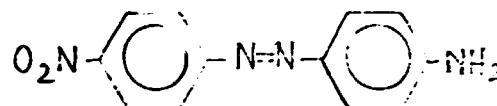
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many non-ionic dyes when dyed in mixtures which suggests that the dye may form an "ideal" solution.

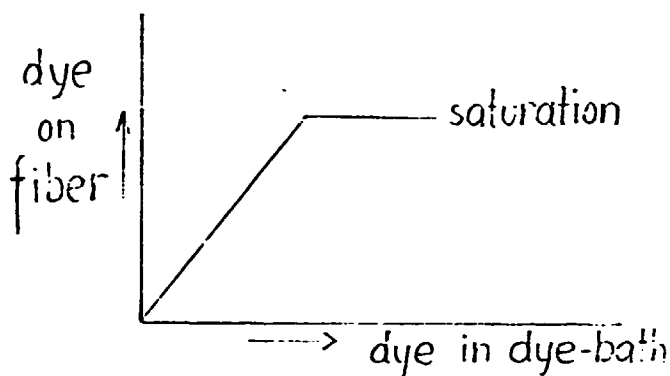


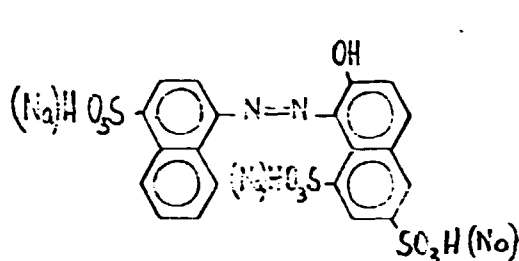
Fig.1 Sorption isotherm of disperse dye on nylon

Polyamides are remarkable uniform to disperse dyes. Even when some of the yarns differ in dyeing rate or dyeability with other dye classes, they seem to be quite alike to disperse dyes. The consequence is that problems of streakiness or barré are seldom serious with disperse dyes, provided that enough time for dye transfer is allowed. For this reason ladies hosiery, dyed in paddle machines or on dye-boarding equipment, is exclusively the domain of disperse dyes because they minimize rings or streaks.

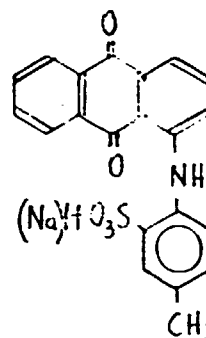
However, there are some deficiencies with disperse dyes. The most serious one is the low fastness to washing. The weak bonding which provides good uniformity of the dyeings, is also the reason for the ease with which the dye is extracted during wet treatments, especially if the temperatures approach the levels employed in dyeing. This shortcoming is of no concern in some end uses, e.g. carpets. In many cases, however, fabrics must be launderable without dye loss. The lack of very bright dyes and dyes of maximum lightfastness is another deficiency with disperse dyes.

2) Acid Dyes (ionic dyes)

Acid dyes can provide good fastness to washing and to light. There are also many bright dyes found with this dye class. For dyeing polyamides either conventional nonmetalized sulfonic acid dyes are used, e.g.

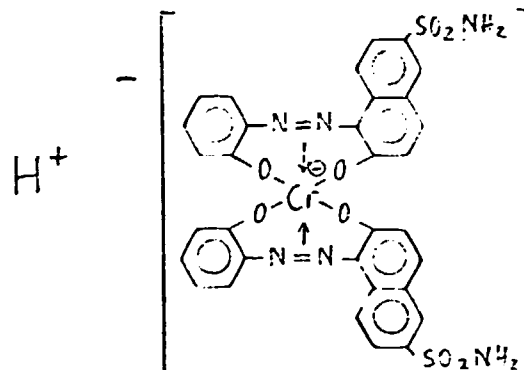


C.I. Acid Red 18



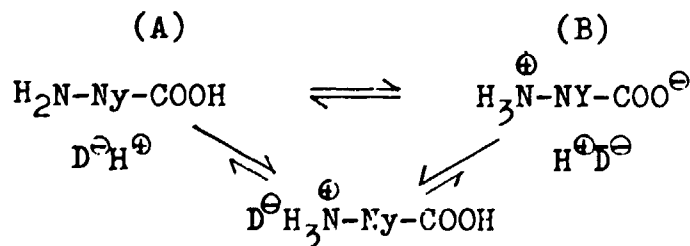
C.I. Acid Blue 78

or premetalized dyes, having structures like



Premetalized dyes are neutral dyeing acid dyes; they are anionic in nature. They normally don't have a sulfonic acid group, the charge is a consequence of the trivalent (+3) metal chelated in a tetravalent (-4) ligand.

Polyamides can be present either as aminocarboxylic acid or as a zwitterion (ammoniumcarboxylate). These two forms are probably in equilibrium



On immersion of the fiber in a dye bath containing acid and dye, hydrogen ions are adsorbed either by the carboxyl group (B) or by the amine group (A). The slowly diffusing dye anion is then able to attach itself to the positively charged amine groups.

The titration curve of polyamide reaches a fairly well-defined maximum corresponding to saturation of the amine groups. However, when the pH reaches 2.5 there is a rapid increase in dye uptake with further lowering the pH, and this increase does not reach a maximum (fig.2)

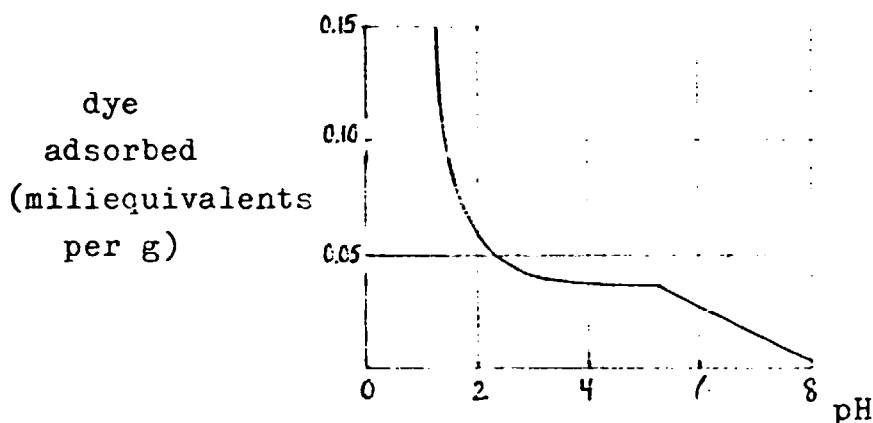
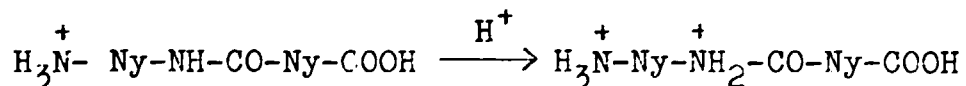


Fig.2 Dye uptake vs. pH

This has been referred to as "overdyeing". Different explanations have been put forward to explain this phenomenon. One theory accounts for protonation of the amide groups.



Another explanation sees a gradual hydrolysis at this low pH and thus formation of new amine end groups. A third hypothesis states that overdyeing by acid dyes at low pH's is due to disperse-type dyeing. Overdyeing should be avoided since it causes a decrease in fastness properties.

Although under normal dyeing conditions the dye uptake is dependent upon the amine end content of the fiber, it

has been shown that not only electrostatic forces are responsible for dye-fiber interaction but also hydrogen bonds and van der Waals forces acting between different groups of the dye molecule and the fiber molecule. These forces are especially effective with the dyeing of premetalized dyes. This class of dyes shows considerable differences with respect to dyeing properties. They exhibit uniform exhaustion properties, low migration characteristics and they are not sensitive toward electrolytes. Further it is possible to dye up to deep shades, no blocking effects are encountered.

But also with the conventional non-metalized sulfonic acid dyes, the van der Waals forces do have an impact on the dyeing process. Actually the acid dyeing has to be considered as a type of ion exchange process. When acid and dye is added to the dyebath, the amine groups of the fiber become positively charged. In a first step these cationic groups form ion pairs with the quickly diffusing acid anions. In a second step the acid anions become displaced by the larger, slowly diffusing dye anions. One can assume that van der Waals forces have a great influence on the displacements.

In the commercial dyeing process there are two important criteria for success: the rate of dyeing and the uniformity of dyeing. Both criteria are influenced by fiber variables (dye site content, molecular weight, surface area) and by dyebath variables (electrolytes, auxiliaries, temperature).

Fiber variables

a) Dye site content

The dyeing rate is greatly influenced by the amine end content since they constitute the driving force for the acid dyeing process. The dye adsorbed increases linearly

as the number of dye sites increases (Fig.3).

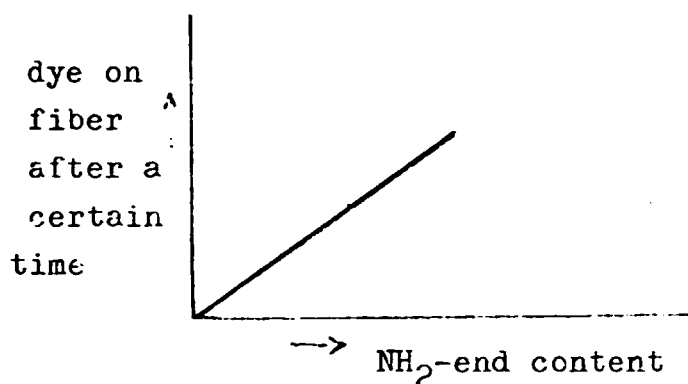


Fig.3 Dye uptake vs. amine-end content

Most commercial dyeings are stopped well before saturation or equilibrium is reached. For this reason it is important that the rate of dyeing is uniform. If some areas of the substrate dye faster than others, a difference in shade will result. Both, the dyer and the fiber manufacturer can influence the rate of dyeing and the uniformity of the rate. Incorporating a larger number of amine end-groups in the fiber will increase the dyeing rate and minimize the dyeing time. However, the result of such an increase in dyeing rate could be a "ring dyed" fiber in which the center is undyed. The dye will diffuse into the center during further processing or washing and the apparent shade will become lighter. A high amine-group content will also decrease leveling during dyeing which could cause uniformity problems.

b) Molecular weight

The molecular weight does not have much influence as long as its value is above a critical magnitude. Above the critical molecular weight many of the physical properties that are related to motion of chain segments, like diffusion, do not change to a considerable extent with a further increase of molecular weight. The segments

are far from the ends and their behavior is determined by their immediate neighbors rather than by the chain ends. Below some critical molecular weight the influence of the ends becomes important. With decreasing molecular weight an increasing dyeing rate will be observed.

c) Surface area

The surface area per unit weight determines the number of sites from which diffusion can start. As the denier per filament decreases the dyeing rate increases. However, denier variations between yarns of a given count are seldom great enough to cause a visible color difference.

Dyebath variables

a) Effect of electrolytes

Especially with sulfonic acid dyes both, the dyeing rate and dye saturation are affected by the presence of salts like NaCl and Na_2SO_4 . The salt anion compete with the dye anion for the dye sites. Salt greatly enhances leveling of streaks caused by variations in fiber physical structure, but decreases dye exhaustion.

b) Effect of auxiliaries

With nonionic auxiliaries a complex is formed with the dye which causes a decrease in mobility. This slows down the dyeing rate and improves leveling without retardation. Cationic auxiliaries are also complexing with the dye in the dyebath. The dye complex is formed at a low temperature. Under the influence of high dyeing temperature, the complex gradually dissociates and the dye ion becomes available to diffuse into the fiber. Anionic auxiliaries depend upon the fact that they compete with the dye for the dye site. By so doing, it is more difficult for the dye to find a point of

attachment. In order to be effective, the dissociation tendency with the dye site in the fiber must be in between the dissociation tendency of the acid anion and the dye anion. When the dissociation tendency is lower than that of the dye, dyeing would be prohibited (reservation).

c) Effect of temperature

Generally, diffusion and therefore the dyeing rate increases with increasing temperature.

Blocking effects

In dye mixtures using dyes of different dissociation tendencies, mutual blocking effects might occur. This effect can be observed when dyes having different degrees of sulfonation are combined. Under the conditions prevailing in the dyebath, the dye of lower degree of sulfonation can be accommodated more readily in any partly occupied region of the fiber than a dye with higher degree of sulfonation.

Causes for uneven dyeings (streaks)

Uneven dyeings with anionic dyes can be due to

- a) physical differences between yarns
- b) chemical differences between yarns

Eventually some physical differences can be found in the fine structure of the polyamide. The fine structure is affected by many operations such as drawing during fiber manufacture, by subsequent operations such as bulking, crimping, heat setting, etc. Variations in fine structure are able to influence both, the rate of dye adsorption and the accessibility of dye sites in the fiber. Chemical differences imply that some fibers may have a different concentration of dye sites than do other fibers. Or that the sites might hold some acid dyes so effectively, that dye transfer cannot be accomplished.

To overcome this problem, level dyeing systems have been developed using selected acid dyes with good leveling properties and leveling agents.

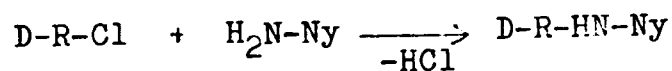
Multicolored effects

Just the opposite of leveling is intentionally made with the production of multicolored yarns. The most important method of obtaining multicolored effects entails the use of nylon fibers with an inherent different level of affinity for either acid dyes or basic dyes. This can be achieved by varying the amine end group content and by the introduction of acidic groups to impart affinity for basic dyes. These developments have been the subject of numerous patents.

3) Reactive Dyes

This class of dyes is not very important for dyeing Polyamides, because they don't have big advantages compared to dye classes already covered.

Reactive dyes form a covalent bond with the polyamide:



D = Dye

R = Reactive System

The dyeing process involves two steps:

- 1) Acid step: dyeing at pH 3-4 with dye and dispersion agent at the boil. At this stage the reactive dye acts like a disperse dye.
- 2) Alkaline step: pH 10 by addition of soda ash. Under these conditions the reactive system reacts with the amine group of the polyamides. As a side reaction there is also a hydrolysis of a portion of dye in the dye bath. The hydrolyzed dye acts like a normal disperse dye, i.e. does not become bound covalently.

Dyeing of Polyester

The polyester fiber with its excellent technological properties is very particular with its dyeing properties compared to other fibers. Polyester exhibits a very low water uptake and a relatively high glass-transition temperature. Therefore higher temperatures and/or auxiliary systems have to be employed in order to get the dye into the fiber. Disperse dyes are used almost exclusively.

Generally polyester dyeing can be divided into two categories:

- 1) Dyeing methods where dye transfer takes place through a liquid phase
- 2) Dyeing methods where dye transfer takes place through a vapor phase

1) Transfer through liquid phase

Disperse dyes exhibit a low solubility in water and a high solubility in polyester. The aqueous dyebath constitutes a low concentrated but saturated solution of dye, in addition to a larger amount of dye being dispersed in the dyebath by a dispersion agent. Only monomolecularly dissolved dye can be adsorbed by polyester. With dyeing times being long enough, a distribution equilibrium is established between monomolecularly dissolved dye in the dyebath and monomolecularly dissolved dye in the fiber. Normally a constant equilibrium coefficient is found, which means a simple Henry (Nernst) distribution, i.e. a linear sorption isotherm. (Fig.4)

Compared to pure dye, commercial dye shows a higher solubility because of the hydrotropic effect of additives.

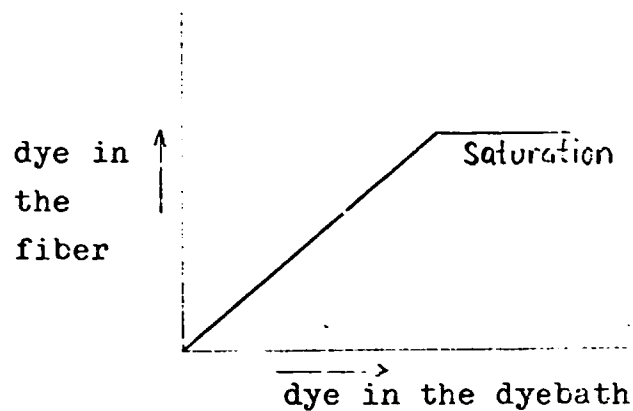
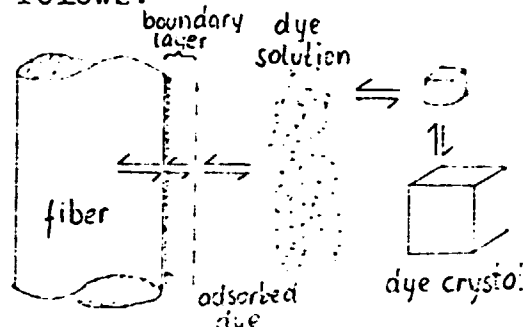


Fig.4 Sorption isotherm of disperse dye on polyester

The energetic situations with disperse dyeing can be represented as follows:



Using a thermodynamic vocabulary: the magnitude of the chemical potential of the dye in crystalline state and the dye in solution must be equal since there is an equilibrium. The change in entropy with the transfer of dye from crystalline state to the fiber surface is small. The driving force must be the loss of enthalpy with adsorption (heat of adsorption must be positive). The adsorbed dye is then diffusing into the fiber because of a gradient in chemical potential. Here the driving force is the gain in entropy.

The rate determining step is diffusion into the fiber. The resistance to the transport of a dye molecule through a fiber arises from two causes. One is due to the forces of adsorption which exist between the dye molecules and the polymer chains, the other one is due to restrictions imposed on the movement of dye by the polymer structure.

Because of adsorption, a fraction of dye present in the fiber is immobilized and is not free to diffuse. However, the adsorption of dye does not modify the characteristics of the diffusion process, since the diffusion coefficient of non-ionic dyes in fibers is constant and independent of dye concentration.

The resistance imposed by the polymer structure is more difficult to describe. Diffusion into fibers takes place at right angle to the axis of the fiber and hence to the polymer molecules. However, dichroic measurements show, that finally the dye is oriented parallel to the fiber axis. An orientation of the dye molecule during diffusion must be considered. The pores of the polyester fiber appear to be even too small to allow entry of dye molecules into the fiber. Since there is almost no swelling in water, the transport must proceed the following way: The dye molecule which is adsorbed to a polymer chain is able to move only if the segmental movement of the adjacent chains is of such a kind that a hole is formed of a size sufficiently large to accept the dye molecule and polymer segments together. Such segmental movements can take place only when the temperature is greater than the glass-transition temperature (T_g). This means that polyester dyeing occurs at a significant rate only when the temperature is raised above this region. Once the T_g has been reached, the rate of dyeing becomes high.

High-temperature dyeing (HT)

In order to be able to dye even heavy shades in a reasonable period of time, machinery has been developed which allows dyeing well above 100°C . The operation can be carried out only under pressure in an enclosed vessel. Temperatures around 130°C are used. With the higher temperatures also the solubility of the dye is increase.

Carrier dyeing

Another possibility to increase the rate of penetration of dyes into polyester fibers is the use of so-called carriers with the dyeing process. Carriers penetrate the fiber in contrast to leveling agents which do not penetrate the fiber but interact with the dye in the bath or at the fiber surface. The carrier causes plasticization of the fiber and lowers the glass-transition temperature. An increase in the concentration of carrier causes a proportional decrease in glass-transition temperature. With the use of carriers even heavy shades can be achieved without using HT-machinery.

Substances which act as a carrier are e.g. o-phenylphenol, biphenyl, methylnaphthalene, trichlorobenzene, etc.

There are, however, certain disadvantages with the use of carriers:

- a) extra cost
- b) difficulty to remove the carrier after dyeing, retention of odor might result
- c) the light fastness is depressed with some carriers
- d) problems with waste water, some of the carriers are very poisonous.

The best results are obtained when carrier and HT-dyeing is combined. The amount of carrier used in HT-dyeing is much lower. The levelness of HT-dyeings is also improved by the co-use of carriers.

Influence of heat-treatment

When polyester is subjected to a heat setting process like thermofixation or texturizing, the crystallinity of the fiber and its glass-transition temperature is changed. This may cause a change in the rate of dye

penetration. The dye uptake of pre-set polyester passes through a minimum with increasing set-temperature.

Streaks and barré

Differences in setting temperatures and in stretching or drawing can give rise to streaks and barré effects. The streakiness, defined as relative difference in the dye take-up of the lighter and heavier dyed material, decreases during longer dyeing times. The leveling depends on the migration characteristics of the dye and on the dyeing temperature. Disperse dyes can be ordered according to their tendency to show up streaks, which makes proper dye selection important. Carrier often enhance streakiness. The best results are obtained with HT-dyeing using little amounts of carrier. This amount has to be small enough to avoid swelling of the fiber. Small amounts increase migration. Also non-carrier auxiliaries exhibit leveling effects in HT-dyeing of polyester.

2) Transfer through vapor phase

With the "thermosol" process dye transfer takes place through vapor phase. The complete process essentially involves the following steps:

- a) application of dye liquor to the fibre by padding;
- b) drying
- c) thermosoling (thermofixing) at 200-210°C, 30-60 sec.
- d) removing of unfixed dye from the fiber surface.

The dye transfer in the thermosol process is very rapid. Therefore it is a very economical method for dyeing textiles containing polyester. Thermosoling is the essential stage in all methods available for the continuous dyeing of polyester/cellulose blends.

Thermal fixation of disperse dyes depends on molecular size and shape, volatility, and solubility of the dye in the polyester fiber. It also depends on the use of heat to open up the polymer structure and make the fibers more permeable to the dye molecules which then diffuse into the fibers.

After padding and drying the dye particles are situated on the fiber in a more or less aggregated state. Under thermosoling conditions the dye vaporizes, i.e. it develops a vapor pressure which is dependent upon its structure and its physical form. The smaller the particle, the higher the vapor pressure. Therefore it is advantageous to use dye pastes (smaller particle size) rather than powders. The vaporized (monomolecular) dye diffuses through a boundary layer, and become adsorbed on the fiber surface.

The next step is diffusion into the fiber. Since the affinity of dye vapor for polyester is very high, the dye-vapor concentration in proximity of the polyester surface decreases almost to zero. This means that sorption takes place instantaneously. Generally it is assumed that the rate determining step is diffusion of dye within the fiber. However, there are doubts to this theory and it has been stated that in some cases diffusion through the boundary layer is rate determining. Actually one can explain the rate of dye transfer by the values of vapor pressure of the dyes used. This corresponds well to the observation that small dye molecules with polar groups, which diffuse rapidly, are good thermosol dyes with good fastness to sublimation, as well as large non polar dye molecules having a very low diffusion coefficient

Factors influencing dye fixation with the thermosol process

a) Fixation temperature and -time

A typical diagram on the temperature dependence of fixation is shown with fig.5

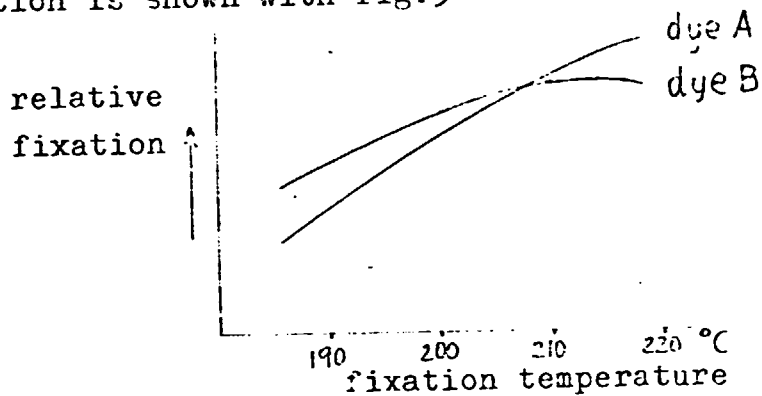


Fig.5 Relative Fixation vs. fixation temperature

With a higher temperature usually more dye is thermosoled up to a limiting temperature. With a further increase, the degree of fixation decreases again. The best temperature is the one where the curve levels off. With higher temperatures shorter fixation times are needed. The dependence of dye fixation by fixation time is demonstrated with fig.6

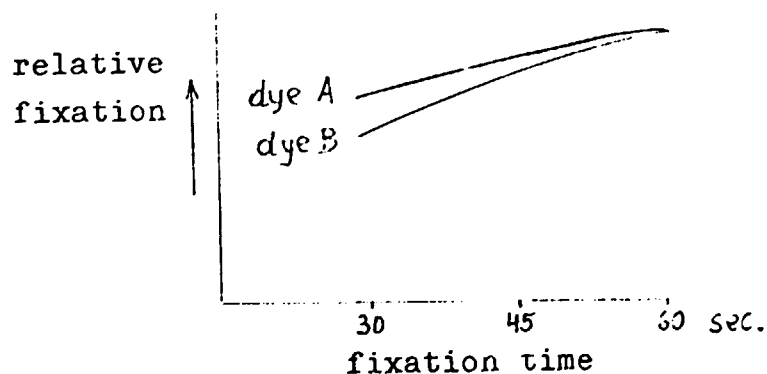


Fig.6 Relative fixation vs. fixation time

The loss of dye due to sublimation in the ambient air is insignificant when the period of heating is very small. It, however, becomes appreciable when the duration of heating is long.

Influence of pH

To obtain maximum fixation a mildly acidic pH (around 6) is most suitable. Increasing OH^- concentration results in decreasing fixation (fig.7)

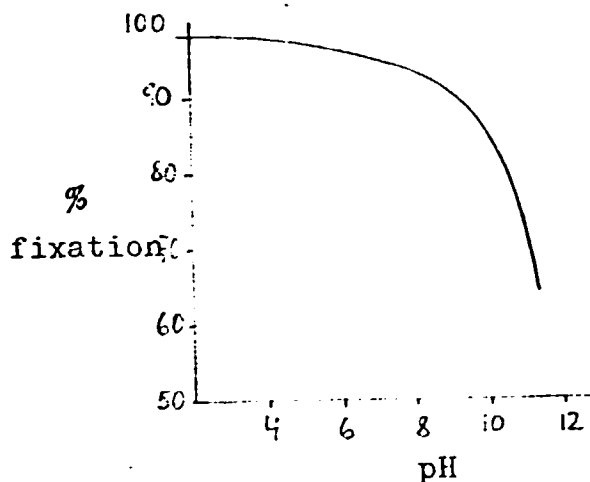


Fig.7 Fixation vs. pH

The reason for this is that only non-ionic dye is capable of being fixed on polyester fiber. As a disperse dye with hydroxyl groups dissociates under alkaline conditions, it becomes anionic and much more soluble in water. The ionic form exhibits a greatly reduced vapor pressure and thus a reduced vapor transfer. Usually monosodium phosphate is added as a buffer.

Migration represser

Control of migration of disperse dye particles in the impregnated fabric during drying is recognized as being of great importance to the success of the dyeing process. Less than optimum dye fixation during thermosoling results if disperse dye has migrated to the fabric surface during drying. This is because not only the surface area of the dye particles is reduced by their agglomeration in the fabric surface, but also the average distance between dye and the total adsorptive surface of the polyester fiber

is increased. Addition of migration represser in the pad effects a decrease in particulate migration. However, there is an optimum in concentration of the migration represser with respect to fixation efficiency.

Structural differences

A big advantage with thermosoling is that structural differences within the fiber (orientation, crystallinity, etc.) don't show up. With the thermal conditions used in dye fixation the crystal structure of the fiber is partly or completely eliminated and replaced by a new one, which, in most cases, exhibits a higher degree of orientation. Thus, it is possible to combine dye fixation and fiber setting in one process.

Dyeing of Modified Polyesters with Affinity for Basic Dyes

The production of basic dyeable polyester is increasing. This type of fiber is used mainly in blends with unmodified polyester in order to get bicolor effects. These effects can be obtained by using selected basic dyes for the modified type which will not stain the unmodified fiber, which in turn is dyed with suitable disperse dyes in the same dyebath.

The dyeing characteristics of the anionically modified polyester fiber is very similar to acrylic fiber. However, the diffusion of a basic dye into the modified polyester is much slower compared to acrylics. The use of carriers is advantageous. The fixation takes place according to an ionic principle rather than by a solution mechanism.

Dyeing of Polyester Blends

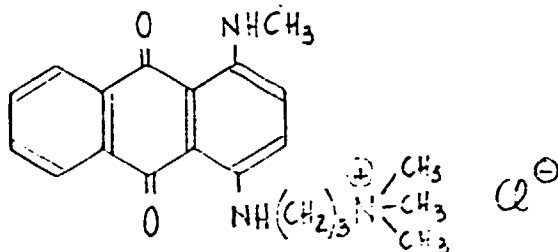
Polyester/cotton blends can be dyed on High Temperature equipment or most efficiently using the Thermosol process. The dyes used are disperse dyes for polyester and dyes for cotton according to the fastness requirements, in most cases vat-, sulfur- or reactive dyes.

With the thermosol process the dye for cotton, usually vat dye, and the disperse dye for polyester are padded together. With thermosoling the disperse dye is transferred from cotton to polyester through vapor phase. The vat dye on cotton is fixed subsequently by a treatment with reducing agent.

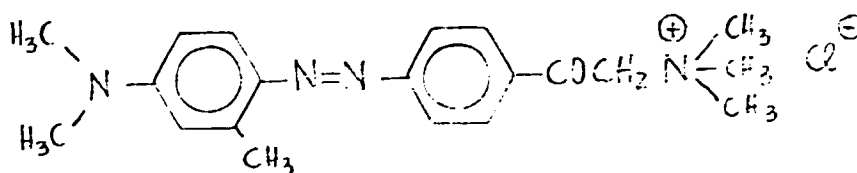
Polyester/wool blends: Premetalized dyes are used for wool. The blend can be dyed using a one bath process or a two bath process. In a two bath process polyester is dyed first.

Dyeing of Polyacrylics

Most acrylic fibers are dyed with basic (cationic) dyes, i.e. dyes that dissociate in aqueous solution to give a positively charged colored ion, e.g.



C.I. Basic Blue 22



C.I. Basic Red 14

Because acrylic fibers contain acidic groups (sulfonate groups) and the dyes used are cationic, the dye-fiber linkage is ionic.

The wetfastness properties of cationic dyes on acrylic fibers are excellent. But also the lightfastness is good to very good. This is surprising considering the poor lightfastness of basic dyes on wool. The explanation for the good lightfastness on acrylics is believed to be the stronger attraction of the sulfonate dye sites compared to the weaker carboxylate sites on wool. The greater the anionic tendency of a site the greater the lightfastness.

The mechanism of dyeing acrylic fibers can be divided into four main steps:

- a) Diffusion of dye through the more or less stationary boundary layer which exists in the solution adjacent to the fiber surface.
- b) Adsorption of dye at the fiber surface.
- c) Diffusion of dye into the interior of the fiber.
- d) Interaction of dye with sites in the fiber.

a) Diffusion through boundary layer

The resistance to diffusion of the boundary layer has no impact on the rate of dyeing provided that adequate agitation is performed.

b) Adsorption on fiber surface

When acrylic fibers are immersed in water, an electrokinetic potential - the zeta potential - is established between fiber surface and water. This negative charge attracts the positively charged dye to the surface of the fiber, where adsorption occurs. At low concentrations of dye in the bath, the fiber gradually loses its negative potential and becomes slightly positive owing to the accumulation of dye cations at the surface (fig.8). When the dye diffuses into the fiber, the potential becomes negative again, and the cycle is repeated.

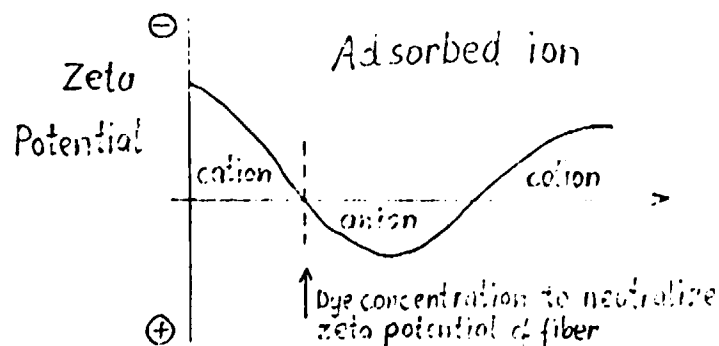


Fig.8 Zeta potential in dyeing acrylics with basic dyes

A further increase in dye concentration above the amount required to neutralize the zeta potential does not change the potential. This is an indication that the concentration of dye at the fiber surface rapidly becomes constant and independent of bath concentration. This is because of the high affinity of the dyes and the limited number of sites available at the surface. The rate of dyeing then becomes entirely diffusion controlled until the bath is almost exhausted. However, dye adsorption does depend on the pH of the dye bath, the use of retarders, the nature of the acrylic fiber, and the basicity of the dye. The effect of pH is due to competition between dye cations and hydrogen ions on neutralization of the surface potential of the fiber.

c,d) Diffusion into the interior and interaction with dye sites

The rate of diffusion of dye molecules into the interior of the fiber is dependent upon many factors arising from the chemical and physical nature of the fiber, the affinity of the dye, and the dyeing conditions.

Only the dye molecules inside the fiber which have not interacted with the sites are able to diffuse. This leads to the conclusion that the basic dye diffuses by a site-to-site mechanism, i.e. dye is transferred from site to site progressively into the fiber. Hence, diffusion depends upon rate of adsorption which in turn is influenced by the nature of the dye molecule and by the number of dye sites. Dyes of high affinity are adsorbed quickly by the surface areas of the fiber, producing ring dyeings. To produce uniform dyeings throughout the fiber, dye must be released by the sites in the surface area or fresh dye liquor must penetrate through the dyed areas to the internal sites. Dyes of high affinity therefore are characterized by their low rate of diffusion in the fiber.

Dyes of low affinity penetrate to the center of the fiber more quickly.

The diffusion coefficient increases with the number of sulfonate groups in the fiber (fig.9).

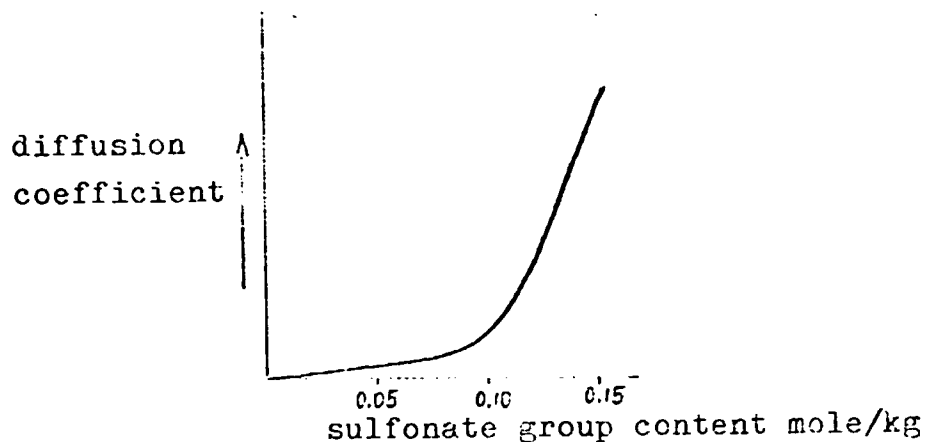


Fig.9 Dependence of diffusion coefficient on sulfonate

Effect of temperature

At low temperatures acrylic fibers have a very compact structure. As temperature increases, the mobility of polymer chains increases. The dye diffusion and therefore the dye uptake is very little below glass transition temperature (T_g). Above T_g the permeability of the polymer increases very rapidly with temperature. The T_g of commercial acrylic fibers differ, but usually it is around 80 - 90°C. Above T_g there is an exponential relation between temperature and rate of dyeing. In proximity of 100°C an increase in temperature of one degree C leads to an increase in the rate of dyeing of about 30%! (fig.10).

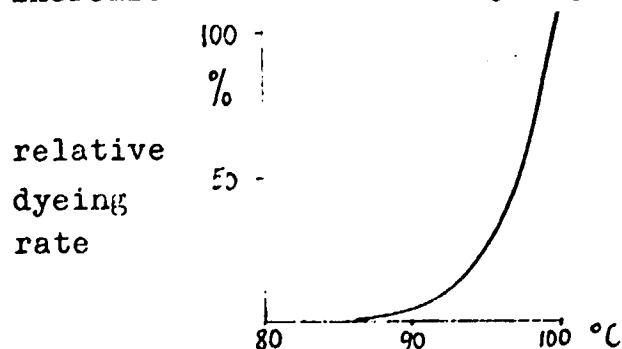


Fig.10 Effect of temperature on dyeing rate

Thus in order to control the rate of dyeing to obtain level dyeings the temperatur of dyeing must be controlled very closely.

Effect of dye concentration

With higher concentration of dye in the bath it becomes easier to produce level dyeings.

The influence of dye concentration in the bath on the rate of dyeing is demonstrated with fig.11

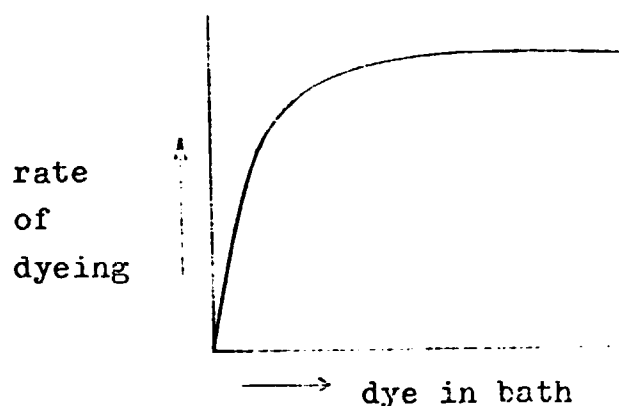


Fig.11 Effect of dye concentration on rate of dyeing

The rate increases sharply initially and then remains constant with further increase in concentration. As a consequence with low initial dye concentration equilibrium exhaustion is attained quickly, and, because of the high affinity of the dyes, leveling problems arise. At higher concentrations of dye in the bath, although more dye is adsorbed initially, the dye remaining in the bath is adsorbed slowly and may cover up unlevelness.

Use of retarders

Owing to their high affinity for the fiber, the migration power of the normal cationic dyes on acrylic fibers is only slight. By means of suitable additives and accurate control of the temperature the dye is adsorbed only slowly

by the fiber. Suitable additives include cationic or anionic retarders.

Cationic retarders have acquired importance in level dyeing. They are colorless watersoluble compounds which compete with the dye for adsorption on the surface of the fiber and for adsorption on the acidic groups within the fiber. Thus they reduce the rate of dyeing.

Anionic retarders are also used which act by complexing with the dye in the bath, thereby reducing the effective dye concentration.

The latest development is the use of polymeric cationic retarders. The multiple charge along the polymeric retarder results in a great affinity for the fiber surface, but, unlike conventional retarders of the same charge, polymeric retarders do not diffuse into the fiber. They remain adsorbed on the fiber surface, where they function throughout the dyeing process.

Behavior of dyes in mixtures

Mixtures of dyes are normally used in commercial dyeing. In order to avoid difficulties with levelness, the dyeing recipes should include only dyes that are compatible with respect to rate of dyeing. As already mentioned, the rate of dyeing is dependent upon concentration. However, the rate determining concentration of a dye in a mixture is not, as might be assumed, equal to the total concentration of all dyes used, even if the concentrations are converted to molar units. A dye behaves differently in mixtures than when applied alone. In order to calculate the dye concentrations needed for dyeing a certain shade, so-called mixture parameters have to be applied. These mixture parameters are dye-dependent values.

Dyeing of Blends

Polyacrylic/wool blends can be dyed using selected basic dyes for the acrylic portion and selected acid dyes or premetallized dyes respectively for the wool portion.

Polyacrylic/cotton blends: selected basic dyes can be used for the acrylic portion. For cotton all cotton dyes are suitable which don't stain the acrylic portion.

One-bath processes can be applied.



