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Chapter 13: Dyeing Blends: Polyester/Cellulose

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Because fiber blends hold an important place in the world's textile marketplace, it would appear highly desirable to be able to classify them all using a single simple classification scheme. However the number of possible blends and blend levels is exceedingly large. Even though the number of blends in general use is considerably smaller, there are still far too many for detailed consideration of all but a few of them within the scope of the present work.

Despite the magnitude of the field, a general basis for examining the dyeing properties of blends has been authoritatively treated by Shore (*1*). The cited work is about 40,000 words in length—equivalent to about 25 pages of Textile Chemist and Colorist—has 130 references and makes mention of 43 binary (two fiber) and 23 ternary (three fiber) blends. The present work will be a small fraction of the size and as a result must be more selective and less even handed. Coverage will have a systematic basis, but the specific blends treated will be guided by the author's preferences, the U.S. market and the need to illustrate particular points.

ABSTRACT

The word blends covers a multitude of possibilities all of which are intentional combinations of chemically or physically different fibrous polymers. Here the concern is with polyester/cellulosic blends.

A number of approaches for coloring polyester/cellulosic fabrics batchwise, continuously or semi-continuously have been examined. These include the application of disperse dyes with azoic combinations, direct dyes, reactive dyes, sulfur and vat colors.

The number of process variants open to the dyer, while dependent on the available equipment, is enormous and the economic success or failure of a program can depend on the right dye and procedural choices being made. Otherwise, it may prove impossible to satisfy the customer's needs and at the same time do it profitably.

KEY TERMS

Azoic Combinations
Blend Fabrics
Cellulose
Direct Dyes
Disperse Dyes
Dyeing
Polyester
Rapid Dyeing
Reactive Dyes
Sulfur Dyes
Vat Dyes

It is estimated that by 1995 ca. 16% of textile fiber consumption worldwide will be in polyester/cotton blends. These presently account for 55-60% of all textile fiber blends, which means that blends account for 25-30% of the world's fiber consumption. Considering that the foregoing chapters have dealt with dyeing single fibers it would clearly be a serious oversight not to discuss the principle fiber blends.

Besides polyester/cotton, typical blends include nylon/cotton, polyester/wool, acrylic/cotton, cotton/wool and more particularly in the U.S., blends of differentially-dyeable nylons, with or without cationic-dyeable nylon, as well as blends of polyester/cationic-dyeable polyester, with or without other fibers. Other noteworthy blends include polyester/nylon, acetate/viscose rayon, viscose rayon/wool and polyester/viscose rayon. Shore's work (*1*) is particularly useful for its inclusion of blends which are infrequently documented in the technical literature.

Perhaps this is the right place to restate (*2*) that while cotton is by far the most important of the cellulosic (vegetable) fibers, the cellulosic fiber category includes a variety of viscose rayons, mercerized cotton and a number of bast fibers from plant stalks. These include jute, ramie and flax, from which the woody (lignocellulosic) materials may be removed to different extents prior to dyeing. Linen is a relatively pure form of flax fibers. The morphology of these fibers may be assumed to be different and they certainly cannot be expected to dye to the same appearance of depth when included together in blends. Blends of different cellulosic fibers will not be treated here. Unless specifically stated, sections involving one cellulosic fiber can be assumed to speak for the others.

What is meant by a blend? What are the purposes of blending?

Definition of Blends

Blends are any textile materials, from fibers (filaments) through yarns to fabrics, which are deliberate combinations of chemically or physically different fibrous polymers. Under this definition blends can range from bicomponent fibers, mixtures of different filaments, core spun yarns, uniformly blended stable fibers through to fabrics which are constructed of intentional mixtures of chemically or physically different yarns—and everything which falls in between.

When the generally known chemically or physically different fibrous polymers are taken two and three at a time, there are a large number of possible combinations. For example, taking only 12 fibrous polymers, there are 66 binary ($11 \times 12 \div 2$) and 220 ($10 \times 11 \times 12 \div 6$) ternary combinations. Since proportions of the polymers in these blends can vary over a wide range to give products with different physical characteristics, the actual number of blend possibilities is unlimited and concern about their number is academic.

Dyeing Possibilities with Blends

The blends, as broadly defined above, may also be dyed to give a number of very different effects:

- Union dyeings: In this case all the components of the blend are dyed to give colors sufficiently close as to be indistinguishable in the finished product; i.e., to give solid shades.
- Reserve or Resist Dyeings: Here at least one (but not all) of the components of the blend remains essentially undyed; i.e., almost white.
- Cross Dyeing: This may be described as deliberately producing fibers of contrasting colors. These contrasts may be strong differences in hue, brightness and depth, but can also be differences in depth only, known as tone-in-tone or shadow effects.
- Cross Staining: This is one of the unwelcome possibilities when dyeing blends, when one (or more) of the components of the blend becomes colored by components of the dyebath to produce a stain rather than a dyeing of generally poor fastness.

One of the keys to the economical dyeing of blends is to be able to get the color effect desired in a total dyeing time less than the sum of the dyeing times necessary to successively dye the components of the blend. This must be achieved without sacrificing quality or operating flexibility within the dyehouse. Processes in which individual blend components are dyed quite separately may be referred to as conservative. Processes in which selected steps of the conservative procedures are run together or eliminated (with resulting time savings) may be referred to as rapid. Clearly, the rapid dyeing processes are of the greatest commercial interest, and they have required the most ingenuity to device. All the major dye companies have their own collections of such processes.

Aesthetics, Economics and Physical Properties

One of the purposes of blending could be to make fabrics which can be dyed to give aesthetic color effects at a late stage of textile production, achieving economies in manufacture. An example would be the blending during needle punching of regular nylon with differentially-dyeable or cationic-dyeable nylon carpet yarns to give tone-in-tone and cross dyeing possibilities.

Another means of combining styling and economic possibilities could be to blend economical fibers with small amounts of luxury fibers into blends such as polyester/viscose/silk or polyester/viscose/linen for the women's wear market. The silk or linen might appear as various types of slubs or nubs in novelty yarns.

Although fibers are blended for the purposes of economics and aesthetics, the most important single reason is to achieve a spectrum of physical characteristics in the blend which is unobtainable using the individual components.

The most obvious and by far the most important example is in the blending of polyester/cotton. The polyester delivers tensile strength, abrasion resistance and dimensional stability, while the cotton delivers reduced pilling, the ability to absorb water and comfort in wear.

The molecules of cellulose in polyester/cotton fabrics can be crosslinked to provide durable press and crease resistant finishes, but in the absence of the polyester the loss of tensile and tear strength (often 30% or more) can be unacceptably high and can effectively rule out otherwise desirable fabrics, such as very lightweight, durable press, 100% cotton shirting fabrics.

The polyester/cotton blends currently account for about one-half of the polyester fiber processed in the U.S. which is why they will be emphasized here.

Interestingly, the different properties of polyester and cotton, which account for the general utility of their blends, turned into a serious drawback when it came to devising suitable flame retardant finishes for such blends (*3*). This is because the different mechanisms of flame retardancy for the two fibers are antagonistic to one another. Cotton forms a carbon skeleton of char and this prevents the polyester shrinking and drawing away from the flame.

Classification of Blends

As was stated earlier, with so many possibilities to choose from, it could be useful to devise a means of classifying blends, and one such method classifies them by the ionic types of dyes necessary to dye the components of the blend to full depths (*1*). In this reference the dyes are divided into anionic dyes (A), cationic dyes (B) and nonionic or disperse dyes (D). Considering the actual blends used to a significant extent in practice, this classification scheme cuts two and three-fiber blends down into only six subdivisions: A, AB, ABD, AD, BD and D.

The principle complication in this system is that there are six categories of anionic dyes and dye precursors, (A), five of which are (almost exclusively) applicable to the cellulosic fibers. The five are the direct, reactive, sulfur and vat colors, plus the naphtholates used in azoic combinations. Only the direct and reactive dyes find significant utility for noncellulosic fibers. Acid dyes are the sixth anionic dye category.

The author will deal with the most important of all fiber blend subdivisions first—polyester/cellulosics. Then in the second half of this chapter, before treating a selection of other significant fiber blends, an alternative system of blend classification will be introduced which breaks down dyes and fibers into four substantivity groups—A-D. In this proposed classification the groups A, B and D are essentially those mentioned earlier except that a new group, C, of anions substantive to cellulosic fibers has been split out of group A, cf. Ref. (*1*).

Regardless of these different classification systems, it is fair to say that the dyeing of each individual blend can be treated separately without the need for classification provided that all the appropriate variables are given due consideration.

Factors Affecting the Choice of Dyeing Methods

The following is a list of factors which dictate the choice of conditions under which particular blends might best be dyed:

- Coloristic effect required (union, reserve, tone-in-tone)
- Colorfastness required of the resultant dyeings
- Suitability of the dyeings for subsequent finishing processes
- Behavior of the different fibers in the blend towards different dyes and dyebath conditions
- Compatibility of dyes from different application categories with one another
- Availability of particular types of batch, semi-continuous and continuous dyeing equipment
- Cost of the dyes and chemicals involved
- Economics of the overall process

Some or all of these points should be involved in any decision to proceed with a particular method of dyeing a given blend.

Polyester/Cellulosic Blends: General

The end use possibilities for the principally 65/35 and 50/50 polyester/cellulosic blended fabrics—ranging from lightweight woven shirtings through a variety of lightweight and middleweight, knit and woven, domestic, apparel and industrial fabrics to heavyweight boat-ducks—are legion.

It is this variety of end uses which makes it necessary for rational choices to be made from the whole armory of products suitable for coloring the cellulosic portion of the blends. These include direct, vat, sulfur and reactive colors, as well as azoic combinations. All of these have been treated separately in Chapters 2 through 6. The pigments, which are so widely used along with resin binders in printing applications or along with cationic modified cellulosics in some exhaust applications, will be treated in a subsequent chapter.

Fortunately the option for coloring the regular polyester fibers in these blends is reduced to the one disperse dye appplication category (*4*). However, there are occasions when cationic-dyeable polyester

About This Series

THIS is the twenty-first installment in this series of papers on dyes and their application. Previous installments have covered the application of anions to nonionic fibers (October 1991), direct dyes (November and December 1991), vat dyes (January and February 1992), sulfur dyes (March and April 1992), reactive dyes (May and June 1992), azoic combinations (August and September 1992), the application of nonionic dyes to fibers (October and November 1992), disperse dyes (December 1992 and January 1993), the application of ionic dyes to ionic fibers (February and March 1993), acid dyes (April 1993), continuous nylon carpet dyeing (May 1993) and basic dyes (June 1993). The series is intended to serve as an introductory text and source book for those who want to expand their understanding of the technology of dyeing and coloration. The author, a frequent contributor to TCC and a member of its Editorial Board, is a professor of textile chemistry at Clemson University.

fibers are also present as a third component in the blend.

When good wetfastness and fastness to thermomigration are required, some prefer to run cationic-dyeable polyester/cotton blends. However, the cost of cationic-dyeable polyester and control in greige mill manufacturing are both problematic.

The cellulosic fiber coloration options can depend on all the factors listed earlier but the principle decisions hinge on which dyes, equipment and procedures to use to produce goods which both satisfy the customer's needs and do so as economically as possible.

Dyes Used for Polyester/Cotton Blends

The following is a brief summary of those basic characteristics of particular dye application categories which are essential to the decision making process. It should be noted that there are considerable variations possible from dye to dye within each category, and individual dye suppliers pride themselves on their ability to advantageously select particular dyes to overcome general performance deficiencies of any dye category. But as a starting point, the following observations are valid.

- Direct dyes are readily water soluble, yield colored anions, are relatively economical, have generally fair to poor washfastness especially in heavy depths and have a color gamut which lacks only the brightest colors, although true greens are scarce. The ease of application is their outstanding characteristic. Washfastness can be improved by post treatments but only at the expense of their ease of application except in the fortunate case of resin finishing.
- Vat colors are sold as powder or paste pigments which in water produce anionic dispersions. The pigments themselves are nonionic but they can (and must be) reduced to water soluble anions in the course of dyeing. The reducing agents are used in the presence of strong alkalis. These alkaline reducing solutions will destroy any available azo dye molecules which are accessible to the solution. Vat dyes are expensive but in return generally have excellent all around fastness. They have excellent light- and washfastness at all depths and have uniquely good resistance to chlorine bleaching. Their color range is somewhat limited. They lack really bright colors and have no neutral reds but have good greens. As a class they are hard to dissolve and not nearly as easy as directs to apply, requiring post oxidation and soaping.
- Sulfur colors are generally sold already in alkaline reduced solutions, in which the substantive color is in an anionic form. They are actually nonionic pigments. They are very economical and in the right circumstances are fairly easy to apply to cellulosics. Some few are sold as pastes or powders which yield anionic dispersions and may be thought of as vat dye hybrids. These require alkaline reduction to render them soluble. They all require oxidation after dyeing. Sulfur dyes have a very limited color gamut, having no true reds, violets or bright yellows. They are excellent for black and very suitable for navy, dark green and brown shades all of which are relatively dull. The washfastness is good, the lightfastness moderate-good, but the chlorine fastness is very poor except for the hybrids. The effluent is generally sulfidinous and if not properly treated can result in bad odors in municipal sewer lines.
- Reactive dyes are intrinsically water soluble, anionic in character and, except for some which use a nicotinic acid leaving group and react under neutral conditions, require various degrees of alkalinity and a range of different temperatures to react with cellulose. If properly applied they have very good to excellent washfastness, relatively poor chlorine fastness and have an extremely wide color gamut. Almost all nonfluorescent shades can be matched with them. They are expensive. Application is normally quite lengthy due to a post-soaping to remove hydrolyzed dye and requires careful control. Reactive dyes require very large amounts of salts to exhaust and generally produce strongly colored very saline effluent.
- Azoic combinations are the most difficult application category of dyes to apply—batch application is rarely used in the U.S.—and even for continuous dyeing the application process is cumbersome. However they are very economical and have very good heavy yellows, oranges, reds, bordeaux and navies, with good lightfastness in heavy depths only. They have very good wetfastness if properly applied and many of them have good chlorine fastness.
- Disperse dyes are sold in the form of pastes or powders which yield anionic dispersions although the very sparingly water soluble dyes are themselves nonionic. Many such dispersions are unstable in the presence of high concentrations of salts. Disperse dyes are sensitive to alkaline hydrolysis—which is why they are normally dyed at pH 4.5-5.5—and the color of many can be destroyed in alkaline reducing solutions. However, once they are within the polyester fibers they are only susceptible to attack under conditions in which the polyester is swollen by aqueous solutions; i.e., well above the glass transition temperature at 70-80C (158-176F). If properly applied they generally have good washfastness.

There are different justifications for the use of colors from any one of the five cellulosic dyeing application categories along with the disperse dyes, and these will be dependent to some extent on whether the dyeing is to be conducted in a batch, a continuous or a semi-continuous process.

In the following sections unless otherwise indicated polyester/cotton woven goods will be used to exemplify the general dyeing characteristics of polyester/cellulosic blends as a whole. The justification for this choice is simple. Woven goods are the most readily dyeable by all three principle types of dyeing process—batch, continuous and semi-continuous—which makes direct comparison between the processes easier. Knitgoods do not have the dimensional stability for treatment on the continuous dye range.

Batch Dyeing Polyester/Cellulosic Blends

There are good reasons why a large proportion of polyester/cellulosic woven goods are dyed on jet dyeing machines at temperatures of about 130C (265F). A primary reason is the elimination of the need for carrier in the disperse dyeing of the polyester. Nevertheless many use carrier for insurance (leveling) often without sufficient concern for the possible consequences. Other reasons include low liquor ratios, rapid polyester dyeing cycles, energy savings and level dyeing due to good dye liquor circulation. Good shade reproducibility is also a plus. More recently, adjustable jet nozzles have been introduced to provide increased flexibility with respect to fabric weights and constructions. Taken all in all, pressure jet dyeing machines are often the machines of choice when batch dyeing woven (and knit) fabrics containing polyester—which includes polyester/cellulosic blends.

As with any other dyeing processes, dyeing polyester/cellulosic blends requires that the goods be suitably prepared for dyeing. Such preparation may include desizing (for woven goods), scouring and bleaching. Mercerizing is optional and not recommended for viscose fabrics. Heat setting for 30-40 seconds at 360-400F (180-200C) can improve dimensional stability, pilling and crease recovery, particularly for heavier weight woven goods.

In dyehouses where goods are treated both batchwise and continuously, all these preparation processes might be carried out continuously. In others the goods may be prepared and bleached in batchwise processes. But there is no call for such processes to be run in pressure machines such as jets. Here it is assumed that the predyeing processes have been completed.

It can be quite confusing to look at published batch dyeing cycle times if one is not aware that some include loading and unloading of the goods, some include batch preparation and bleaching. Others are strictly the time from the beginning to the end of the dyeing processes proper; i.e., no loading, no unloading, no finishing. But washing-off, oxidation, soaping-off and other steps are included, if necessary to the proper development of the dyed shade. This latter convention is used here. Note that the times of draining, refilling and making adds should not be ignored, since they are quite significant.

Batch Procedures for Disperse/Direct Dyes

Once it has been decided that the desired shade and fastness properties can be met using direct dyes for the cellulosic portion of the blend, there are two principle dyeing options.

• Conservative/Two Bath: The polyester is dyed in the jet at 130C (265F) which requires about 160 minutes. The next stage is reduction clearing to clear the cellulosic fibers of any disperse dye staining and to destroy any particulate disperse dye on the polyester surfaces which process is followed by a further pH neutralization step. This stage requires about 90 minutes. Direct dyeing of the cellulosic portion at ca. 90C (195-200F), followed by two cool rinses, requires a further 210 minutes, which completes the dyeing cycle proper in about six hours.

The whole process could be split into two baths to maximize the utilization of the jet dyeing machine. The reduction clearing could be foregone with pale shades.

The washfastness of the cellulosic portion of such dyeings is improved by the same resin finishing which (conveniently) is used to assist shrinkage and dimensional stabilization of knitgoods and which is also used for durable press or crease resistant finishing of most polyester/cellulosic woven goods. These finishes are not generally used for 100% cotton fabrics because of the unavaoidable tensile and tear strength losses incurred. The finish may include cationic or cationic resinous direct dye fixatives and softeners, although their use may adversely affect both the shade and the lightfastness of some direct dyes.

• Rapid Dyeing/One Bath: The disperse and direct dyes are added at the start and the temperature raised to 130C (265F) to dye the disperse dye. The high temperature not only causes the direct dye to dye the cellulosic portion very rapidly, but is conducive to leveling or stripping and at equilibrium gives a lower dye partition coefficient—i.e., less dye in the fiber and more in the dyebath than at lower dyeing temperatures. The temperature is then lowered to ca. 82-90C (180-195F). For some dyes—e.g., C.I. Direct Black 22—the pH may be adjusted to 8-9, Glauber's salt added and the exhaustion of the direct dye is completed at an appropriate temperature. The bath is then dropped at temperatures from 60-70C (140-160F) and the goods are given two cool rinses. The total dyeing time should be about four hours; i.e., a time saving of two hours compared with the conservative procedure.

The economic gains associated with the rapid dyeing process must be weighed against the constraints imposed by this process. The limitations are that the direct dyes must have high temperature stability and the disperse dyes must show no cross staining and need no reduction clearing because reduction clearing would destroy the direct dye as well. Dyes are available such that these constraints can be met.

Thirteen high temperature stable directs are listed (*5*), which fall primarily in class B but with class A and class C dyes represented (*6*).

Certain disperse dyes are noted for their cross staining characteristics: e.g., C.I. Disperse Reds 65 and 338 and C.I. Disperse Blues 56 and 79. These dyes give dyeings on polyester/cotton blends whose staining on cotton and nylon during the AATCC 2A Wash Test (*7*) show considerable improvement—1.5-2.0 points on the five-step AATCC Grey Scale for Staining—if they are first reduction cleared.

For both dyeing options the disperse dyes selected should neither migrate nor desorb readily under the influence of resin finishing or in the presence of softener. This holds true regardless of which class of dyes is used for the cellulosic portion of the blend. Although the potentials for migration and desorption are intrinsic properties of individual disperse dyes, the products and procedures used in finishing can materially affect the fastness properties of the resultant goods.

Batch Procedures for Disperse/Reactive Dyes

It has been shown that disperse/direct dye combinations result in savings of time, energy, labor and payback costs when compared with disperse reactive combinations (*8*). However, if brilliant shades and high wetfastness are necessary then direct dyes will not fill the bill; e.g., in sales yarns. Both direct dyes and reactive dyes have problems with very dark shades. Dark direct dyeings have poor wetfastness; dark reactive dyeings can be very expensive.

The alternative (nonconservative) dyeing processes for disperse/reactive dyes on polyester/cellulosics parallel those for disperse/direct combinations except that the number of possibilities is far greater. There are several reasons for this but the main one is that now there are advantages to both dyeing the polyester first or dyeing the cellulosic portion first. The variety of reaction conditions for fixing different types of reactive dye only complicates an already complex situation.

Using the same approach as given in the previous sections there are four principle types of processes by which polyester/cellulosic fabrics can be dyed with disperse/reactive dyes (*9*). There are also many special variants designed to take advantage of particular properties of special dye products. Any procedures indicated here are intended to be generic and should in no way be construed as favoring reactives dyes of any particular reactivity or chemical type.

The biggest stumbling block to shortening reactive dyeing procedures is the absolute necessity for complete removal of the hydrolyzed dye from the cellulosic fibers (*10*) (see comments later).

• Conservative/Two Bath: Here the polyester is dyed by the preferred procedure, the goods are reduction cleared, the cellulose is dyed by the preferred procedure and the hydrolyzed reactive dye is removed by scouring. These steps are independent of one another.

There are few restrictions on the choice of disperse and reactives dyes used except that the combination meets the desired color and fastness requirements. The problem is that the total dyeing process time is in the order of nine to ten hours of which about two hours is devoted to scouring. Clearly this is far too long to tie up a high temperature machine when temperatures above 100C (212F) may only be necessary for about one hour.

• Less Conservative/Reverse Two Bath: Here the reactive dye is dyed first and the scour is reduced to a couple of warm rinses to remove alkali and salts prior to a conventional disperse dyeing cycle. It is this polyester dyeing cycle which is utilized to provide the scouring necessary for removal of the hydrolyzed reactive dye.

Now the cycle time is reduced to about seven hours but there are some restrictions. Since there can be no reduction clearing (because it would destroy the fiber reacive dye), the disperse dyes must be carefully selected to show minimal cross staining and residual color on the polyester surfaces. However, some companies produce disperse dyes which clear during an alkaline scour only (*11*).

It may also be necessary when using some reactive dyes to elevate the disperse dyeing pH to 6-6.5 to obviate acid hydrolysis of the cellulose-dye bonds (Cell-O-Dye) formed.

• Rapid/One Bath: Here disperse dye and reactive dye are added first and the pH buffered to ca. 6.5. The Glauber's salt is added when the temperature has been raised to about ca. 80C (175F). The temperature is raised to 130C (265F) to dye the polyester, dropped for the addition of alkali to complete the dyeing of the cellulosic fiber and the goods are scoured.

It can be seen that careful selection has to be exercised to find dispersions which will not be cracked by the addition at large amounts of electrolyte (salts). The pH of maximum stability of the reactive dyes must be chosen and controlled with care. The disperse dyes selected must not cross stain cellulose or remain on the polyester surfaces after dyeing, because no reduction clearing is possible.

The potential reward is the reduction of the dyeing cycle time to just over five hours. But without excellent consistency and control over the process the risks are real enough. Another possible alternative is:

- Rapid/Reverse One Bath: Here the dyebath pH is suitably buffered—e.g., to pH 9.0-9.5—and the temperature raised to 125C (250F) with simultaneous dyeing of the reactive and disperse dyes. These conditions will be very dependent on the particular reactive dye type selected. However, few disperse dyes are stable at the slightly alkaline pH, which limits the choice. The method relies on increasing the reactivity of the reactive dyes by raising the temperature rather than by the conventional method of raising the pH.

Again, restrictions in dye use apart, the reward is a dyeing cycle proper of just over five hours.

Clearly disperse/reactive dyeing cycles can be brought down fairly close (within about 90 minutes) to those possible for disperse/direct dyeing cycles, but only with some limitations in dye selections and the need for great control. For many dye houses the question is not so much one of whether the potential benefits of rapid dyeing processes are desirable but whether day to day reliability and reproducibility of shade and fastness properties can be achieved.

Scouring Off Hydrolyzed Reactive Dye

The author finds himself unable to leave the subject of reactive dyes without some comment on the length of time required in practice to remove hydrolyzed reactive dye from cellulosic fabrics. It would seem that somewhere between the variables of the hydrolyzed dye substantivity and its rate of stripping, the scouring liquor ratio, the temperature of the wash water, the frequency and duration of dropping and heating the scouring baths, the design of the dyeing machines and positioning of the drain, and others, there should be a series of recommendations for minimizing the time and cost of this lengthy process.

The information is available and its public dissemination is overdue. See for example Ref. *(13)*.

Batch Procedures for Disperse/Vat Colors

As sold, disperse dyes and vat colors are remarkably similar. Once added to water, they both yield very fine anionic dispersions of essentially nonionic colors. In neither case has the color significant water solubility at ambient temperatures.

Polyester/cellulosic fabrics in the presence of disperse/vat color combinations are carried through a conventional disperse jet dyeing cycle at pH ca. 5 and a dyeing temperature of 130F (265F). Additional anionic surfactant is usually added to help stabilize the dispersion and to disperse any other sparingly soluble material which might be extracted into the bath. It is normal to add sequestrants to tie up any calcium or magnesium salts present in cotton cellulose or in the water.

While the disperse dye is dyeing the polyester, the vat dispersion is prepigmenting the cellulosic fibers. It should not be too surprising to discover that some of the vat colors stain the polyester quite heavily. After all, the simpler vat color molecules do have structures very similar to those of anthraquinonoid (AQ) disperse dyes: e.g., C.I. Vat Yellow 3.

Some manufacturers have sold vat/disperse combinations selected to minimize cross staining for dyeing union shades. Their commercial success has been limited by cost and the number of polyester/cellulosic blend levels used in practice.

The batch is then cooled to no more than 85C (185F) but generally from 60-70C (140-160F) and caustic soda (ca. 30 g/L) and hydro (ca. 10 g/L) are added. The temperature of 85C (185F) is higher than normal dyeing temperature for many vat dyes and is too high for some indanthrone blues, which are sensitive to over-reduction. However, it does facilitate leveling. Reduction clearing of the polyester and reduction of the vat color to its substantive, water soluble, sodium leuco form occur simultaneously.

Dyeing is continued for about 30 minutes, often at a reduced temperature, followed by rinsing, oxidation, soaping at the boil *(11)* and final rinsing. The cycle lasts about four to five hours depending on the depth of shade, and is capable of yielding a range of shades of excellent light- and washfastness at all depths. However some vat colors are unsuitable and others require sodium nitrite to be added (ca. 3 g/L) to prevent over-reduction. Disperse/vat dyeing is best performed in closed machines such as fully flooded jets or beams because of the rate of air oxidation of the hydro. Some vat colors perform better when added after the dyebath temperature has been lowered from 130C (265F), but this extends the cycle because the goods need at least 15 minutes for prepigmentation at the lower temperature.

Batch Disperse/Sulfur and Disperse/Azoic Procedures

The procedures here are conventional, conservative and therefore time consuming. Nevertheless some sulfur dyes, blacks in particular, are so economical and give such outstanding depths of shade that the length of the double process is tolerated. Disperse dyeing normally precedes the sulfur dyeing in a two-bath, two-step process. This way the alkaline reducing conditions in the sulfur dyebath will assist in clearing the disperse dye. The other way around would require careful neutralization of the sulfur dyebath residuals to ensure that they did not affect the disperse dyes, particularly under high temperature conditions.

There is little call in the U.S. for the three-step process of applying disperse/azoic combinations batchwise *(13)* but there are still areas of utility for these combinations in continuous dyeing.

Continuous Dyeing Polyester/Cellulosic Blends

Dyeing polyester/cellulosic woven fabrics is the specific purpose for which the pad-dry-thermosol-chemical pad-steam range was designed. Given sufficient yardage of goods, outstanding results are achieved with vat, sulfur and reactive dyes for the cellulosic portion of the blend. Although not as common, direct dyes are also used. Azoic combinations, mainly reds, are sometimes selected despite the need to run goods through parts of the dye range with two passes.

Most of the continuous polyester/cellulosic dyeing methods can be considered conservative in that the front end of the dye range is specifically designed to dye just the polyester portion of the blend by thermofixation of the disperse dye. The disperse dye is applied to the goods (along with antimigrants) in the first pad, predried, dried and is then caused to sublime into a monomolecular form in the thermosol oven, when it has high substantivity for polyester fibers. After 30 to 60 seconds in the thermosol oven at 200-215C (390-420F), the dyeing of the polyester is complete. It only remains to clear residual disperse dye from the fiber surfaces by means of the subsequent alkaline and reductive treatments which result from the pad-steam phase of the continuous process during which reactive sulfur or vat dye anions diffuse into the cellulose.

The continuous applications of the various cellulosic dye application categories have already been considered; i.e., direct *(6)*, vat colors *(11)*, sulfur colors *(14)*, reactive dyes *(10)* and azoic combinations *(13)*.

The most intriguing aspect of continuous dyeing is the way in which application technology has been developed to make life easier for those in the dyehouse. For example, vat colors are applied as pigment dispersions along with the disperse dyes in the first pad. The goods pass through predrying, drying and then thermofixation where some of them inevitably stain the polyester quite heavily. Next the goods run into a caustic and hydro reducing pad bath of low volume and at high speed prior to entering the steamer. The difficult drugroom problem of producing standing baths of reduced vat dyes and the problem of differential strike rates out of a pad bath containing highly substantive reduced vat dyes are simply sidestepped by the dyeing process. Direct and reactive dyes which are heat stable are also applied in the first pad. They emerge from the thermosol section of the dye range dried onto the cellulose but not yet dyed. They then pick up salt or alkali plus salt respectively in a low volume pad trough before steaming. Again, strike rate problems are essentially done away with.

The day to day production dyeing problems which have not been completely solved are elucidated in a landmark paper by Smith and Melton (*15*). They examine the causes of creasing, as well as problems which arise at the dye pad, in predyeing, in the thermosol unit, at the chemical pad, in the steamer and in the washboxes. Fifteen problems are analyzed for their causes and cures are suggested. Some additional information is available (*16*).

All in all, if the fabric is right and the yardage sufficient, continuous dyeing has a lot to commend it.

Semi-Continuous Dyeing Polyester/Cellulosic Blends

The most important semi-continuous method of dyeing cellulosic fibers and their blends with polyester is the cold pad batch method. This method requires little capital investment since it requires only a suitable dye pad, insulated batching trucks or beams, equipment for washing-off the resultant dyeings (*10*) and plenty of polyethylene sheeting. At this time, the method has been found exceedingly valuable for use with fiber reactive dyes, where the goods are padded with dye and alkali, batched, wrapped in plastic to exclude the possibility of drying, and neutralization of caustic alkali by CO_2 in the air, and left in a constant temperature environment until the dye-fiber reaction is judged to be complete. This is normally about 12 hours but can vary widely. The procedure is completed by a washing-off cycle. Cold pad batch may be used for the application of selected direct dyes also, and it has been proven useful for bleaching.

Direct dyes which are suitable for cold pad batch are those which are highly concentrated and largely salt free (*17*) and which have good solubility in cold water although they are still dissolved in hot water. Those which are highly aggregated in cold solutions will have difficulty diffusing into the cellulosic fibers. To help ensure the presence of enough dyes in the nonaggregated monomolecular form, it is customary to add 25-50 g/L urea. An anionic wetter is included to assure uniform penetration of the pad liquors, which are adjusted to a slightly alkaline pH (8-8.5) to aid dye solubility.

The customary small pad trough will largely eliminate tailing effects in dye mixtures. The batching process generally takes somewhere in the order of 15-20 hours.

The low labor costs, low water and energy consumption and the flexibility to dye long or short production runs coupled with good shade reproducibility make cold pad batching a very attractive process, for both reactive and direct dyes, particularly since it can be equally useful for tubular knit, open width knit as well as woven flat goods.

The method can be used to dye the cellulosic portion of blended goods which have already had the polyester portion dyed in the jet (with or without reduction clearing) or alternatively it can be used to dye the cellulosic portion of blended goods. It has even proved successful in dyeing greige knit goods for subsequent dyeing of the polyester in the jet. However, in the latter case, the polyester cannot be reduction cleared after dyeing.

As far as blends are concerned, the greatest utility of cold pad batch is still for dyeing fiber reactive dyes on cellulose, while freeing up pressure dyeing machines for rapid HT polyester dyeing cycles.

Review

The word blends covers a multitude of possibilities all of which are intentional combinations of chemically or physically different fibrous polymers.

The number of such blends is academic but between them they constitute 25 to 30% of the world's fiber consumption. Of them, polyester/cellulosic blends (but more particularly polyester/cotton) are easily the most commercially important. Blends can be made for aesthetics, economics or improving the physical properties of textile materials.

Dyeing blends is a challenge because the different polymers involved (almost by definition) will not have the same level of substantivity for the same application categories of dyes. The chemical conditions for application of one category of dyes might even destroy the dyes of a different application category.

A number of possibilities for coloring polyester/cellulosic fabrics batchwise, continuously or semi-continuously have been examined. These include the combinations of disperse dyes with azoic combinations, direct dyes, reactive dyes, sulfur and vat colors.

The number of process variants available to the dyer, partially dependent on the available equipment, is enormous. The economic success of a program can depend on selection of the right dye and procedures. Otherwise it may prove impossible to satisfy the customer's needs and at the same time do it profitably.

An extensive general reference to the dyeing of polyester/cellulosic blends is Ref. (*18*).

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