Appendix A

Problems With Fiber Reactive Dyeings Not Repeating - A Look at Five Typical Cases

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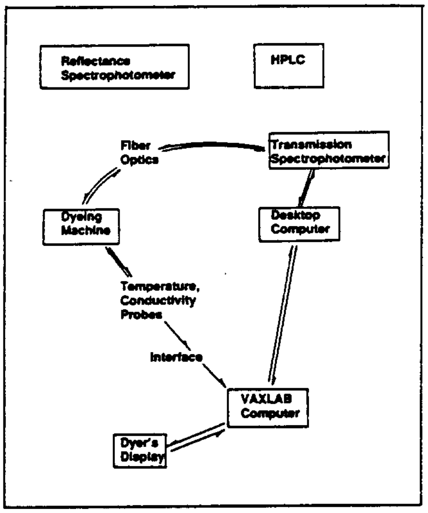
Introduction

While it's a fact that the fiber reactive dyeing of cellulosic materials is of great commercial importance, it is also one of the most difficult batch processes to control. As part of a Consortium for Research in Apparel, Fiber and Textile Manufacturing (CRAFTM), the authors have developed a system for acquiring real-time on-line data from batch dyeings. Actual production dyeing problems can now be diagnosed in our own laboratory using data from this data acquisition system. This information is a great asset to both laboratory and production dyers in establishing dye recipes and procedures which, due to their inherent design, repeat consistently and resist shade variations.

The data acquisition system is described in more detail elsewhere[1,2]. Data from this system include information about dye concentration in the dye bath at any time, conductivity, pH and temperature. In addition to diagnosis of dyeing problems, these data can be used for other purposes such as modelling and studying dyeing processes, and real time process control.

The system consists of sensors to detect pH, conductivity, temperature, dye and chemical concentrations in the dyebath on a real time basis; signal conditioners; micro and mini computers; displays and peripherals, as shown in the block diagram in Figure 1. We have used this apparatus to examine dyeing recipes and procedures with exceptional production history (good and bad). Data from such dyeings show exactly why some dyeings "went wrong," and also indicate how to improve the performance of these shades in terms of the dye procedures and recipes.

Figure 1—Data acquisition system.

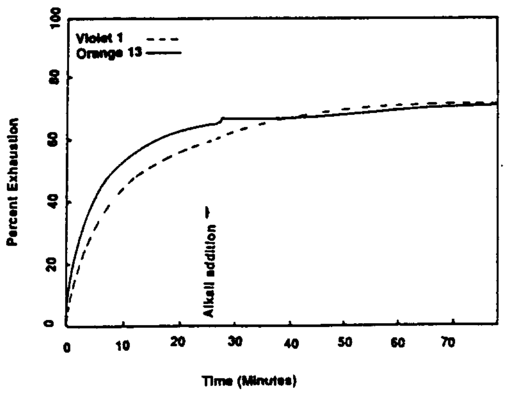


To control fiber reactive dyes, one must consider many important factors, such as diffusion, reactivity and substantivity. In addition, there are important differences between types which must be taken in account. These differences are graphically demonstrated by our real-time data acquisition system.

Case I: A "Normal" Dyeing with Triazines

Dyeings known to have good production history generally use dye combinations with similar exhaustion and substantivity characteristics. A typical case is shown in Figure 2 for a combination of two monochloro triazine dyes, Orange 13 and Violet 1. The kinetics of exhaustion as well as the substantivity of the dyes clearly produce similar exhaust curves up to the time of alkali addition (25 minutes). Addition of alkali, which in this case produces essentially no further exhaustion of the bath, initiates the reaction phase of the dyeing. The overall reaction rate is controlled by several factors: concentration of dye present, concentration of nucleophile (i.e., cellulose or hydroxyl anions), and reaction rate constant. The fixation efficiency depends on the relative reaction rate of

Figure 2—Dye exhaustion vs. time—Violet 1 and Orange 13.



the dye with cellulose compared to water, which in turn depends on the relative amounts of dye in the fiber and in the dyebath respectively. Note that, at the time of alkali addition, exhaustion has essentially reached a steady state, thus the timing of the alkali addition is not critical. Also, the exhaustion is moderate to high for fiber reactive dyes—about 60% at the time of alkali addition. Under these conditions, reaction of the dye with the fiber occurs reproducibly and efficiently.

Case II: Triazine Dyes of Different Substantivity

Figure 3 shows another combination shade of two monochloro triazine dyes, Yellow 135 and Blue 5. As in case I, exhaustion of each dye has reached a relatively steady state prior to alkali addition. But in this case, the yellow component is nearly 80% exhausted at the time of alkali addition, compared to just over 40% for the blue.

This has important practical implications to the dyer because the relative efficiency of fixation of the two dyes will depend on their relative reaction rates which in turn depend on their relative concentrations in the fiber. Even with all other factors (e.g., reactivity of the dyes) being equal, the fraction of blue dye in the fiber is about half as great, giving much lower fixation efficiency and more hydrolysis. Thus, the "hot patch" taken before washing will contain much more unfixed hydrolyzed blue dye, which will wash out and the shade will wash down to a more yellow cast. The dyer will be faced with a hot patch decision requiring considerable judgment as to how much the shade will change on washing.

Case III: Alkali Added Too Soon

Figure 4 shows a combination of two dichloro triazine dyes, Yellow 7 and Blue 4. Although alkali was added after the same time (25 minutes) as in the two previous cases, the data clearly indicate that, in this case, dye is still exhausting. Therefore, the timing of the alkali add has a great effect upon the ultimate shade. If alkali is added slightly earlier than specified, more dye will remain in the bath and thus relatively less of the dye will be fixed. Control of the alkali add must be almost exact, since any deviation in the timing of alkali addition or even at the time it takes to circulate the alkali throughout the dyeing machine could well produce shade variation. Other factors (e.g., fabric preparation, temperature/rate of rise, salt concentration) might well advance or retard dye exhaustion slightly, and thereby significantly affect shade repeatability.

In cases I and II exhaust to a steady state existed prior to alkali addition. For those processes, ultimate dye exhaustion depends primarily on the final conditions in the exhaust phase, e.g., temperature, salt concentration and liquor ratio. Momentary fluctuations do not substantially affect the final exhaustion. But, in this case, dye continues to exhaust after the addition of alkali, giving simultaneous exhaustion and reaction. The dyeing results then become highly path dependent and any fluctuation in the factors previously mentioned is likely to result in a poor shade repeat or unlevel dyeing. This is a higher risk situation and requires more careful control to achieve good shade repeats.

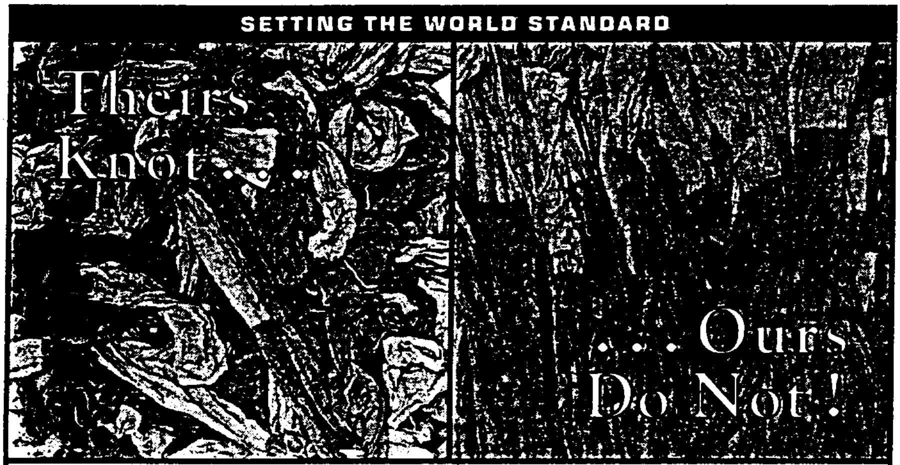


Figure 3—Dye exhaustion vs. time—Yellow 135 and Blue 5.

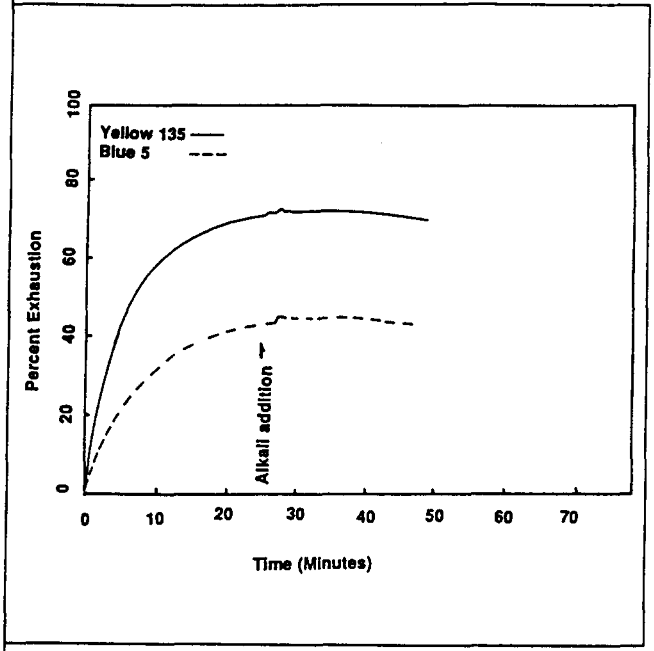


Figure 4—Dye exhaustion vs. time—Yellow 7 and Blue 4.

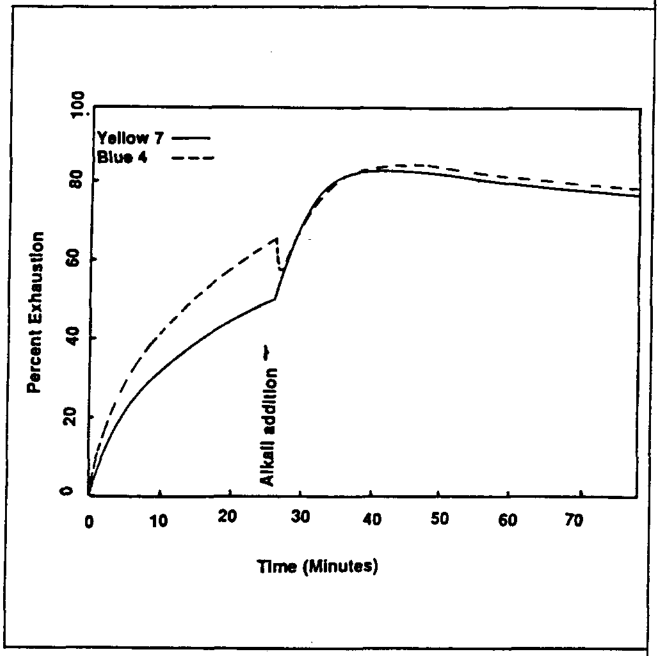


Figure 5—Dye exhaustion vs. time—Blue 3R and Blue 21.

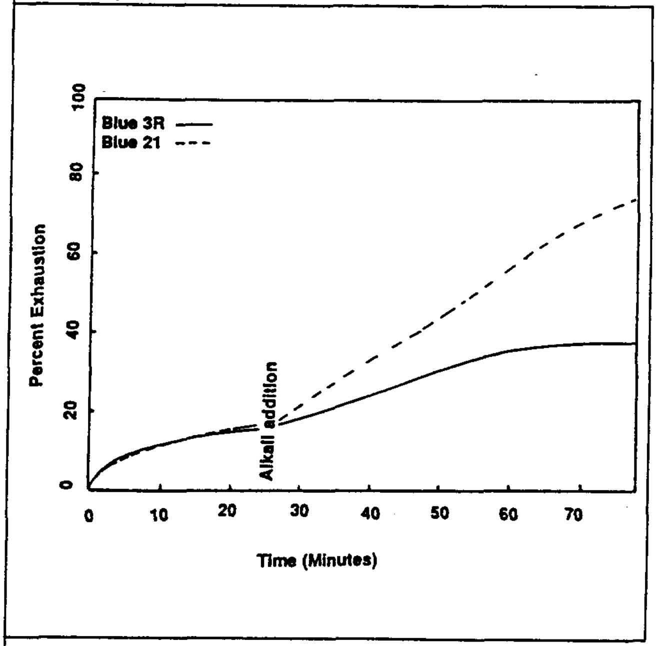
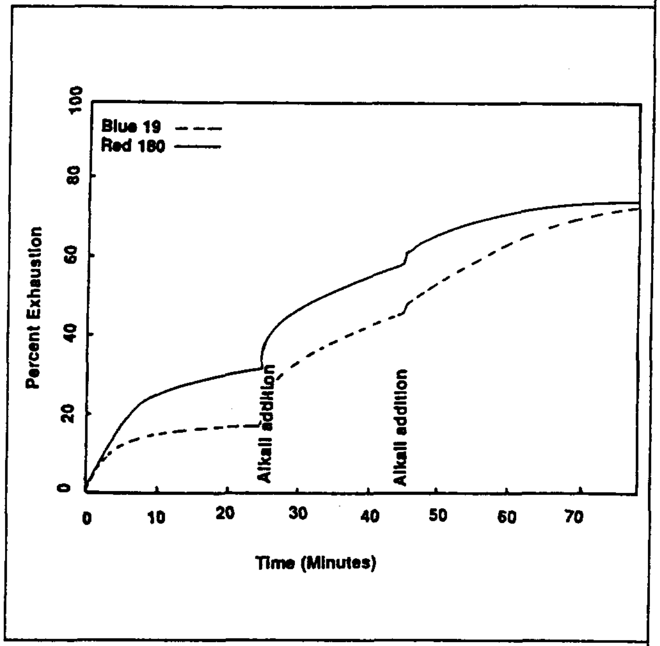


Figure 6—Dye exhaustion vs. time—Blue 19 and Red 180.



Case IV: Vinyl Sulfones of Different Reactivity

Figure 5 shows the performance of a combination of two sulfatoethyl sulfone dyes, Remazol Blue 3R (no C.I. Number) and Blue 21. (Note—due to pH sensitivity of the dyes in this recipe, a scale factor adjustment was made at the time of addition of alkali.) These dyes have very compatible exhaustion prior to alkali addition and reach a fairly steady state. But, in contrast to the triazine dyes described in the preceding, these dyes commence exhaustion again after alkali addition. This is typical of the vinyl sulfone types, and is due to the elimination of the sulfato group and the formation of the less soluble (higher affinity) reactive vinyl form. Blue 21 continues to react and exhaust for some time after the Blue 3R reaches its final exhaustion level. Thus, the final shade is affected by the total dyeing time and any delay in dropping the dyebath is likely to produce a shade variation. Also, the comments made in case II regarding wash down and in case III concerning simultaneous exhaustion and diffusion apply.

Case V: Different Substantivity

Figure 6 shows a combination of Blue 19 and Red 180. In this case, the alkali was added, in parts in an attempt to control the dyeing. But the data clearly show the incompatibility of the dyes in terms of substantivity. After the addition of alkali, the blue component is exhausting at a greater rate than the red, leading to a situa-

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tion similar to cases III and IV. This requires careful control of many factors, e.g., temperature and alkali addition, to achieve good shade repeats and level dyeings.

Conclusions

Fiber reactive dye formulations and procedures vary greatly in their performance. Even if dyers had essentially perfect control over their processes, shade variations would still result from uncontrollable factors such as fiber maturity, ambient conditions, water quality, dye and chemical variances. Therefore, it is important to devise dyeing protocols which are highly resistant to variations. Situations which lead to inherently unstable shade repeats can be identified by examination of dyebath data. Dye recipes and procedures which are high risk can be identified in advance using real time dyebath data acquisition.

In these studies the authors successfully identified several specific situations leading to higher risk of poor shade repeats in fiber reactive dyeing as demonstrated by these cases. A few of the most prominent problems included (a) selection of dyes of different affinity or reactivity and (b) addition of alkali too soon. ☐ ☐ ☐

References

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(2) Beck, Keith, Madderra, Tod and Smith, Brent, Real-Time Data Acquisition in Batch Dyeing, in press, Proceedings of the 1990 AATCC National Technical Conference and Exhibition.

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[Continued from page 75]

sumer the diversity of product mix for styling and differentiation.☐☐☐

(1) J. Gordon Cook, Handbook of Textile Fibers 2. Man-made Fibers, p. XXVIII.

(2) C. H. Giles, The Theory of Coloration of Textiles, p. 41.

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News
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Acquisition Agreement

Cromptön & Knowles Corp. Stamford, CT, recently announced it has signed a definitive agreement to acquire the business and certain assets f Atlantic Industries, Inc., a Nutley, J based producer of dyes for the xtile industry.

Although details of the proposed nsaction were not revealed, C&K did announce that the acquisition would be made for cash and is expected to be completed in the third quarter of 1990.

Atlantic Industries, Inc., is an indirect, wholly-owned subsidiary of Great American Management and Investment, Inc.

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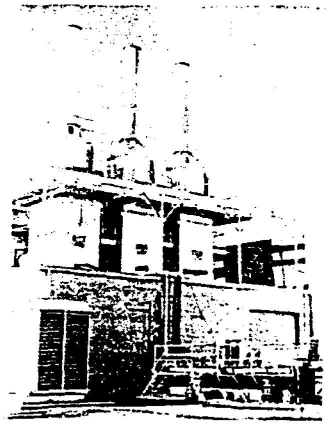


Troubleshooting In Dyeing—Part I: General

By Dr. Brent Smith, NC State University, Dept. of Textile Chemistry, Raleigh, NC

Second in a series of ten articles by Dr. Brent Smith on the theme, "Troubleshooting In Dyeing."

Troubleshooting of dyeing problems is a difficult task because so many variables are involved and because observers are very sensitive to minor variations in dye application. This article, Part I, reviews several important factors that apply to dyeing in general, including:

Basic dye theory;
Color standards and shade guides;
Color judgments;
Raw material and substrate variation;
Automation;
Dyestuff quality control; and,
Standard test methods.

Parts II and III will deal with specifics of batch dyeing and of continuous dyeing, respectively.

Dyeing - The Basics

Before getting into specific details of problem solving in dyeing, it may be helpful to briefly mention some basic concepts of dye theory. Two important and fundamentally different branches of dye theory should be understood, which are:

☐ Kinetics (Mechanisms, Rates);
☐ Thermodynamics (Equilibria, Isotherms).

To be a successful dyer requires knowledge and understanding of how these elements are affected by managing various parameters, as well as the ability to apply these principles then to the practice of dyeing. There are several basic dyeing mechanisms, as shown in Table I.

Some of these mechanisms are used by exhaust dyers, i.e. distribution, affinity, and (less often) entrapment. Others, especially entrapment and binding, are often used by continuous dyers. The exhaust dyer attempts to produce an even, reproducible shade by diffusion, migration, and subsequent fixation of dye in a substrate through an approach to equilibrium conditions. Three types of equilibrium dyeing behavior are represented by the three dyeing isotherms shown in Figures 1, 2 and 3.

Figure 1

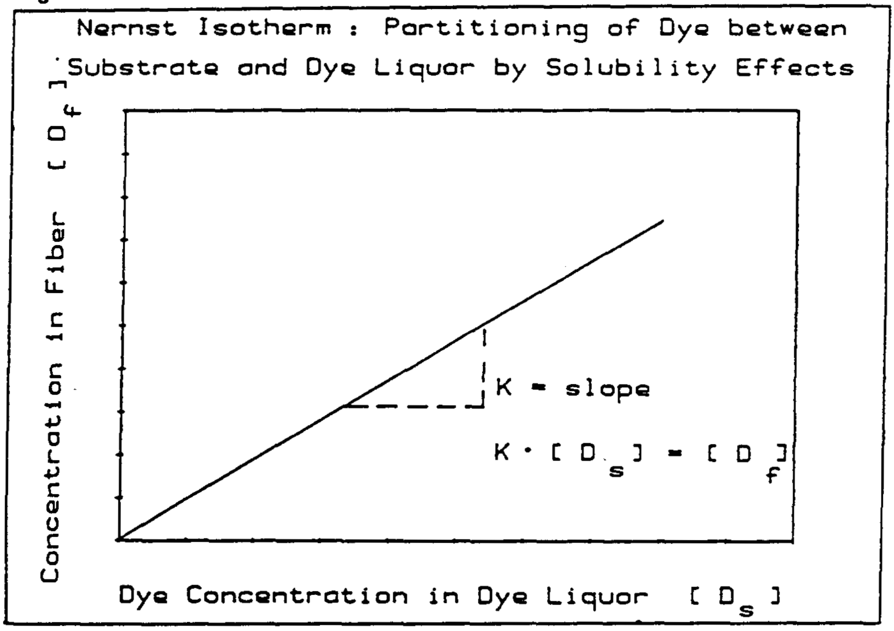
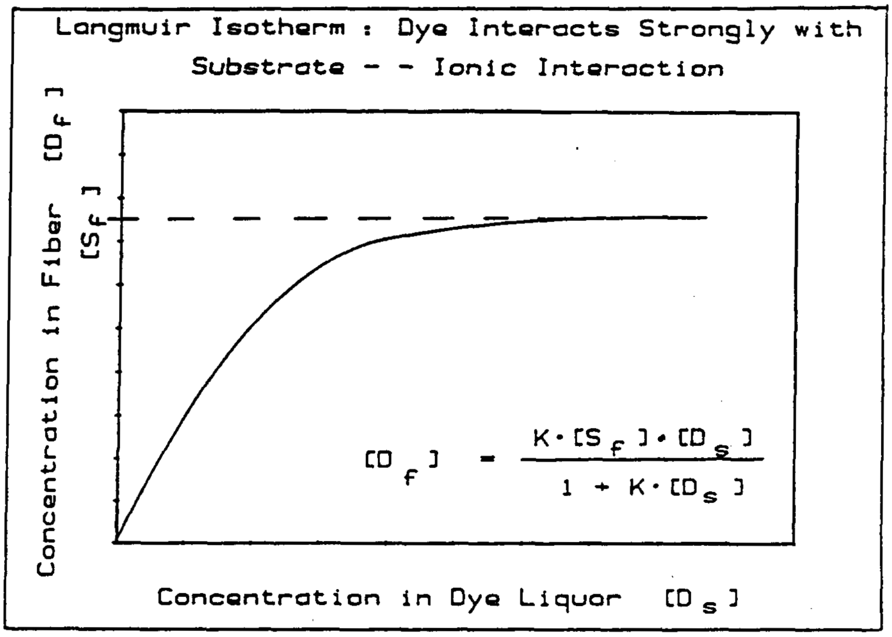


Figure 2



These isotherms and dyeing mechanisms represent varying physical situations which exist with particular fiber/dyestuff combinations, as shown in Table II. They are affected in differing ways by pH, electrolyte, dyeing auxiliaries, and temperature. Each isotherm expresses a relationship between equilibrium concentrations of dye in the fiber $[D_f]$, dye in the dye liquor $[D_s]$ also, dyesites in the fiber $[S_f]$, and constants (N,K) which are characteristic of the system. These isotherms represent specific equilibrium conditions and are influenced by many specific factors for different dye classes. Control of these factors is essential for consistent dyeing. These will be reviewed on a class-by-class basis in Part II.

In commerce, the equilibrium, which is represented by the isotherm, is never fully attained. Thus, another critical factor for the exhaust dyer is the kinetics or rate of dyeing, as shown in Figure 4. This rate must be carefully tailored to the isotherm specifics of the equipment, dye, and substrate. Exhaust curves express the rate of exhaust in terms of the ultimate (equilibrium) percent of dye which will exhaust (E_∞) as well as the time $(t_{1/2})$ required to obtain half of that amount of exhaustion. Exhaust curves are non-equilibrium data based on percent exhaust (amounts, not concentrations) of dye. Control of many critical factors which affect $t_{1/2}$ is essential for good shade repeats and level dyeings. The shape of these exhaust curves will depend on dyeing conditions, variations in temperature, electrolyte, pH, etc. These considerations will be discussed in depth in Part II.

The continuous dyer, on the other hand, depends on uniform wetting followed by fixation or binding steps done under non-equilibrium conditions. To produce even dyeings in this situation, a dyer gives careful attention to mechanical details as well as chemical reactivity, penetration of dye, etc. Critical parameters for the continuous dyer will be discussed in Part III of this article, "Troubleshooting in Continuous Dyeing." Control of shade and evenness of dyeing requires attention to different details, depending on whether the application is exhaust (batch) or continuous.

Figure 3

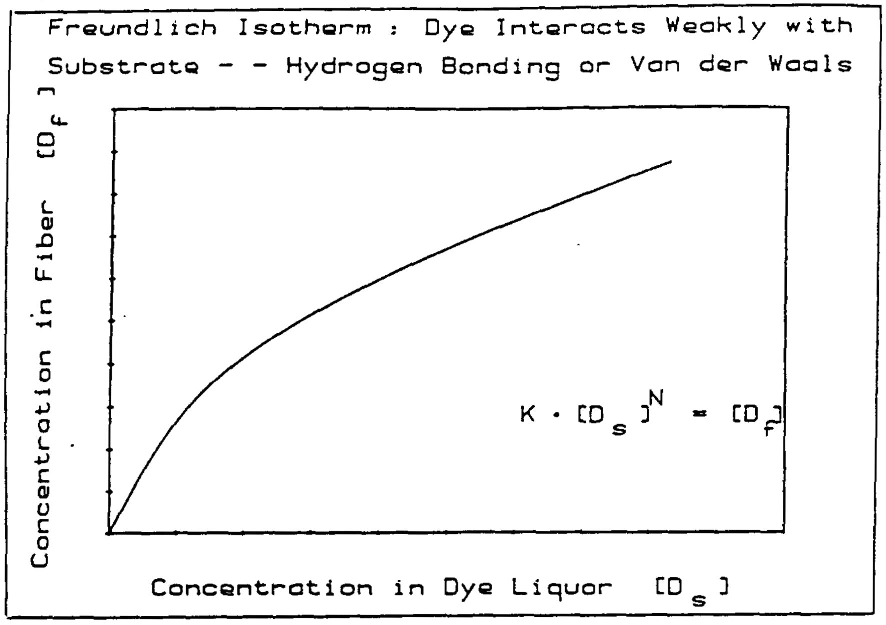
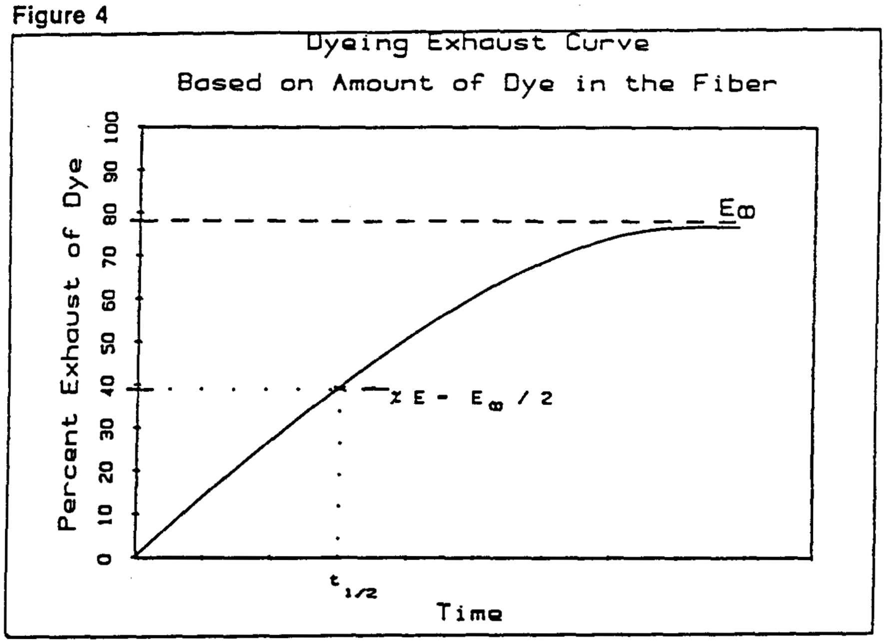


Figure 4



Color standards and shade guides

One critical area in dyeing quality control is the selection, establishment, storage, and use of color standards. Since the human mind has relatively poor ability to "remember" color, color standards (physical or numerical) are universally used by dyers for judgment of dye lots. Of course, the judgment is no better than the sample taken from the dye lot. It is also no better than the standard. Having a good standard as well as a good sample from the lot is critical for both instrumental and visual shade judgments. What constitutes a "good" standard depends on many factors.

At this point, it is important to define the distinction between a "color standard" and a "shade guide." The color standard is a primary standard which could be any physical object or numerical specification for a particular color. Color standards are necessary in the development of new shades and coordination of different component parts.

A shade guide, on the other hand, is a secondary standard of a particular dye recipe on a specific substrate in a certain state (for example, finished or not finished). The use of shade guides greatly facilitates both instrumental and human color judgments by avoiding certain problems. One such problem is possible metamerism between the color standard and production lot sample, which can result from differences in dye recipes. By using shade guides (instead of color standards), metamerism and the effects of lighting variations are minimized. Problems arising from observer metamerism are also reduced. Furthermore, potential problems arising from appearance differences between the color standard and lot sample such as nap or other surface finish, luster, gloss, and haze are reduced. The use of shade guides also improves performance of instrumental color judgments.

An ideal shade guide is a full-scale, no-add production dyeing of a particular recipe on a specific substrate. Less desirable situations include (from "better" to "worse"):

Lab dyeings (same recipe/substrate);

Sample production lot (short run or partial load);

Rehandled production lot, "topped up," or lot with dye add;

Different substrate and/or recipe; and,

Non-textile material.

In addition to the preceding, the manner of drying and conditioning is critical for both the shade guide and lot sample. Drying temperatures, times, tensions, and surface contact can cause considerable shade variation between samples. Tensions and contact (such as with steam heated drying cans) may cause a change in the surface appearance of samples because of surface fusing, thermal bulking, shrinking, or stretching of the substrate. The use of gas-heated drier vs. electrically heated vs. hot cans may give different shade changes.

Finishing recipes should be consistent between shade guide and lot sample, especially with respect to catalysts, which may cause shade changes in cellulosic and other dyes, and with respect to softeners which may be fluorescent or may contain fluorescent brighteners.

Color Judgments

Having obtained an adequate shade guide and lot sample, one must then make a comparison of the two for some purpose, such as accepting or rejecting the lot. This can be done instrumentally or visually. The practical details of how to make instrumental color judgments are reported in the literature.[1,2] Usually, especially in cases of problems or disputes, visual color judgments will be the deciding factor. It is amazing that many processors who rely heavily on visual color judgments usually have no documented standard procedure for making a visual color judgment. Many companies have standard lighting surroundings. Some even have standard presentation methods and color testing for observers. Few, if any, have specific instructions for observers with regard to other factors involved. Important considerations for visual judgments of small color differences are described in the literature.[3,4] These recommended practices should be understood by each person who makes critical commercial color judgments.

A different set of considerations applies, however, when comparing video displays to textile materials, for example when using computer aided design systems. An excellent review of this subject is available and should be studied carefully by anyone who makes use of CAD/textile color systems.[5] Since color vision is not instantaneous, and because of successive contrast effects, the time of the observation as well as the "resting" time between successive observations is important. Also, long term fatigue plans an important role in color judgment if an observer works for several hours.

There are many factors which must be carefully controlled in order to make color judgments which are reproducible and correlate with the more important factors in perceived color:

-Illumination;

-Sample preparation and presentation;

-Surroundings;

-Observer; and,

Table 1: Mechanisms of Dyeing

1. Simple distribution of dye between the substrate and dye liquor (non-ionic)
2. Specific affinity of dye for fiber by hydrogen bonding, Van der Waals forces, or ionic interaction which may occur at specific sites, by electrical effects, or formation of bonds.
3. Mechanical entrapment of dye within fiber.
4. Binders which hold pigments in place on the fiber surface.

Table II: Physical Mechanisms, Dyeing Behavior, and Isotherms

Dyeing mechanism	Fiber/dyestuff example	Observed behavior isotherm
Simple distribution	disperse/synthetic	Nernst
Specific affinity	Acid/wool	Langmuir
	Acid/nylon	
	Basic/acrylic	
	Direct/cellulose	Freundlich
Entrapment	Vat*	None*
	Sulfur*	
	Naphtol*	
Binding	Pigment	None

*Exhaust dyers apply certain types of dyes in a two-step procedure, in which the exhaust phase (described by an isotherm) is followed by a reactive phase not described by any isotherm.

Table III: AATCC Test Methods Relating to Preparation[1]

Test number	Property
20 and 20A	Fiber Identification
97	Extractable Materials
78	Ash Content
79	Absorbency
144	Alkalinity of Substrate
81	pH of Substrate
82	Fluidity
17,27,43	Wetting
89	Mercerization
98	Alkali in Bleach Baths
102	Peroxide in Bleach Baths
103	Enzyme Activity
149	Chelates
110	Whiteness

Intangibles.

Consistent color judgments are not difficult to achieve. However, it is surprising how often the following fundamental ground rules are overlooked, leading to problems.

Illumination is usually well controlled in dyeing and laboratory environments, but not in other environments, such as *cut-and-sew* areas or meeting/conference rooms. Normal color matching is usually done under daylight, incandescent, cool-white fluorescent, and/or Ultralume® lighting. Techniques, equipment, and effects of varying lighting are well known. Lighting should be controlled in spectral energy content, level or intensity, and diffusion.

Shade guides and color standards should be handled and stored carefully.

Exposure to light, burned-gas fumes, and other atmospheric contaminants can cause changes in color. Also, residual chemicals in paper and plastic holders cause changes in color of a stored sample, if the sample comes in contact with them. Normal use of shade guides causes them to become stretched, dirty and abraded, causing a change in appearance and color. Therefore, shade guides must be monitored and replaced when necessary. The frequency of replacement will depend on the amount of use, physical properties of the guide, and how carefully the guide is handled. Sample and guide presentation should be consistent in orientation, size, viewing distance, conditioning, edge contact and preparation. Surroundings should also be controlled carefully. The usual procedure is to use a flat-gray surrounding of about 18% reflectance, corresponding to a photographic gray card or a Munsell® color designation of N6 to N7.

Another critical factor in color judgments is the observer. There are substantial differences between observers with "normal" color vision. These differences go beyond the gross colorblindness detected by pseudoisometric plates. These differences are subtle and typically include to regions of low color discrimination and/or observer metamerism, which may be detected and quantified by use of the Munsell-Farnsworth Hundred Hue Color Discrimination Test® and the Glenn Color Rule®, respectively.

Table IV: Defects and Latent Defects Which Come from Preparation[1]

Defect	AATCC test method
Residual waxes and oils	#97 Extractable Materials
Silicate deposits	#78 Ash Content
Uneven absorbency	#79 Absorbency
Residual alkalinity	#81 pH and #144 Alkalinity
Fiber damage	#82 Fluidity
Poor bleach base	#110 Whiteness and #78 Ash Content
Resist (oxycellulose)	Several Methods[6]
Poor mercerization	#89 Barium Number
Residual peroxide	Spot Test[7]

Table V: Dyeing Defects and Water Contamination

Inconsistent shade:
- Chorine
- Iron and copper [sensitive dyes]
- Calcium and magnesium [poor washing off]

Blotchy or streaky dyeings:
- Alkalinity or acidity
- Residual alum from city treatment systems

Filtering, spots, resist:
- Sediment
- Organics
- Metal hydroxides, fatty acid complexes

Table VI: Thin-Layer Chromatography[5]

Dye class	Developer system	Solvent proportions	Adsorbent
Acid	n-Butanol/Acetone/Water/Ammonia	5:5:1:2	Silica Gel G
	Methyl Ethyl Ketone/Acetone/Water	2-4:1:1	Silica Gel G
	n-Butanol/Ethanol/Water	1-2:1:1	Alumina G
Basic	n-Butanol/Ethanol/Water/Acetic Acid	9:1:1:0.1	Silica Gel G
	n-Butanol/Acetic Acid/Water	2:1:5	Kieselguhr
	Pyridine/Water	1:2	Silica Gel G
	Ethanol/Water	5:2	or neutral Alumina
Direct	n-Butanol/Methanol/Ammonia/Pyridine	4:1:3:2	Silica Gel G
	Propanol/25% Ammonia	2:1	Silica Gel
	Pyridine/AmylAlcohol/25% Ammonia	1:1:1	Silica Gel
Disperse	Toluene/Acetone	20:1	Silica Gel
Solvent	Chloroform/Hexane/Acetone	3:1:1	Silica Gel
Naphthol	Chloroform/Acetone	9:1	Silica Gel
	Methanol/Methyl Ethyl Ketone	5:2	Silica Gel
Reactive	Butyl Acetate/Pyridine/Water	2:2:1	Silica Gel
	n-Butanol/Pyridine/Water/Ammonia	5:5:3:2	Silica Gel
	Propanol/Ethyl Acetate/Water	6:1:3	Silica Gel
Metallized (2:1)	Chloroform/Ethanol/Morpholine	8:1:1	Silica Gel

These tests have been administered to hundreds of students in academic and extension courses at NCSU and the differences which are commonly detected between "normal" observers is surprisingly great. Furthermore, observers usually find it hard to believe that everyone does not see color the same. Thus, it seems only reasonable that every person who is associated with commercial shade developments should be tested on a frequent basis. This is rarely done in commerce, perhaps because many color professionals are reluctant to take these tests.

There are other modifying factors related to color vision beyond observer differences. These include fatigue, impairments, successive and simultaneous contrast effects, and intangible "acceptance" criteria that have been learned by the observer.

Intangibles include social background or other factors. Examples of such "other factors" in color judgments which frequently influence color judgments in production situations are perspectives of individuals, such as:

-Quality control manager: Who is the customer?

-Plant manager: When is the lot due out?

-Dyer: What are the chances that reworking the lot will make it better? These factors can never be completely eliminated from color judgments.

Raw materials and substrates

The two fundamental sources of product variation are raw materials (including substrate) and processing. It is not possible to properly optimize processing conditions and equipment while important raw material or substrate variation is significant. This is especially true in dyeing operations. Control methods for chemical specialties, chemical commodities, and the substrate itself are presented in other parts of this series.

As to the effect of preparation upon dyeing, the key is consistency. Several standard tests for fabric preparation are shown in Table III. Properly administered and interpreted, these tests will detect defects and latent defects which can affect dyeing processes. Particular defects and contaminants which freqently result from improper or inadequate preparation are also shown in Table IV, with tests to detect them. Specific situations relating to these are discussed in other parts of this series.

Water quality, as discussed in detail in other parts of this series, has a profound effect on dyeing. While specific effects vary, common causes and effects are shown in Table V.

The limitations of dyeing machinery require one's particular attention, especially with respect to compatibility with substrates. In many cases, nothing can be done to avoid problems arising from the above, but sometimes these problems can be overcome by improved preparation. Even when nothing can be done to improve compatibility between substrate and equipment, knowledge of the limitations allows for increased quality control checks and proper cost factors, based on anticipated high off quality and seconds levels.

Automation

One trend in modern dyeing practice is the use of automated microprocessor controls for dyeing equipment. These controls, if properly maintained and calibrated, can be of great assistance to the dyer. However, there is a tendency for dyers who use automated equipment to spend less time on the dyehouse floor actually observing the dyeing processes. In fact, automated controllers can lull a supervisor or dyer into the false sense of security that all is well.

There is no substitute for the dyer's personal observation of processes running on the floor.

One look at an unexhausted dyebath or unusual color of water draining from boxes of cloth recently unloaded from becks or jets can be very revealing in terms of spotting potential problems, which automated systems can not detect. This personal presence and observation of production processes is important in batch or continuous dyeing, as well as in preparation and in finishing.

Table VII: Paper Chromatography[5]

Dye class	Developer system	Solvent proportions
Acid	Ethanol or Methanol/Water	4:1
	t-Butanol/n-Butanol/Water	4:3:3:
	n-Butanol/Ethanol/Water/Ammonia	2:1:1:1
	Methyl Ethyl Ketone/Acetone/Water	2-4:1:1
Basic	Methanol/5N Ammonia	8:2
	Butanol/Acetic Acid/Water	2:1:5
	Pyridine/Water	1:4
	Butanol/Ethanol/Water	1:1:1
Direct	Butanol/Pyridine/Water	2:3:3
	Benzyl alcohol/DMF/Water	3:2:2
Disperse	Chloroform/Acetic Acid/Water (on Silicone treated paper)	1:1:1
	Pyridine/Water	1:3-5
	Tetrahydrofuran/Water or N HC1 (on Acetylated paper)	80-54
Reactive	2% Na_2HPO4 in 5% Ammonia	—
	Butanol/Water/DMF	11:11:3
	Butanol/Acetic Acid/Water	2:1:5
Vat or Sulphur	10% Tetraethylenepentamine/$Na_2S_2O_4$	10:1
	Ethyl Acetate/Ethanol/Water (on acetylated paper)	1-2:1:1
Metallized (2:1)	n-Butanol/Formic Acid/Water (on Whatman DE-20 paper)	5:1:2
Acid (1:1)	Acetic Acid/Water	3:2
Acid (2:1)	Tetrahydrofuran/0. 1N HC1 (on 80% acetylated paper)	80-:54

Table VIII: Developing Solvents Polarity: Elutive Power[4]

	Solvent	Dielectric constant
non-polar (less elutive power)	m-Hexane	1.9
	Petroleum ether	2.0
	Cyclohexane	2.0
	Carbon tetrachloride	2.2
	Benzene	2.3
	Tetrachloroethylene	2.3
	Toluene	2.4
	Trichlorethylene	3.4
	Diethyl ether	4.3
	Chloroform	4.8
	Ethyl acetate	6.0
	Phenol	9.8
	Pyridine	12.3
	iso-Propanol	18.3
	n-Propanol	20.1
	Acetone	20.7
	Ethanol	24.3
	Methanol	32.6
	Acetonitrile	37.5
polar (more elutive power)	Water	78.5

Dyes

There is, at this time, no comprehensive standard AATCC test method for quality-control testing of dyes, although procedures are being developed by committee RA98. However, it is necessary for dyers to have some method of determining whether

Table IX: AATCC Methods Relating to Dyeing[1]

Test Number	Property
26	Aging of Sulphur Dyed Cloth
161	Effects of Chelates in Dyeing
153	Instrumental Color Measurements
Various	Fastness (25+ Tests)
141	Basic Dye Compatibility
146	Disperse Dye Filtering
140	Dye Migration
139	Thermosol Disperse Dyes on Polyester
159	Acid Dye Transfer
156	Basic Dye Transfer
155	Disperse Dye Transfer

or not incoming dyes are inadequate for their needs. The following procedures are not necessarily related to the work of committee RA98, but are simply suggestions to the practical dyer of some methods which may prove useful.

For each dye in use, it is good practice to have not only the OSHA Form 20 (MSDS) as required by law, but also the manufacturer's technical data sheet and a physical standard. Standards should be stored in a cool, dark, dry place and should be replaced or updated as recommended by the dye manufacturer. A good quality control scheme for a dyehouse is to sample 50 to 100 grams of each dye as received and send to the laboratory for testing. A satisfactory laboratory evaluation comprises:

- solubility or dispersion;
- color value by either transmission or dyeing;
- thinlayer, or paper, chromatography;
- special tests for unique dyes;
- viscosity, density, and specific gravity for liquids;
- retain sample for future reference; and
- proper documentation.

Drums which are suspected of causing problems or which have been opened for a long term should be resampled and retested.

Solubility or dispersion can be easily tested by standard methods such as AATCC Test Method 146. Color value of a dye can be determined by transmission measurements after dissolution in an appropriate solvent. However, this does not measure certain important properties of a dye such as substantivity and/or fixation properties. Therefore there is merit in the practice of evaluation by actually dyeing a substrate with the dye from the drum and with the dye standard. Results of dyeings may not be directly comparable between different mills, because different dyers use different procedures and because of even slight variations in water quality. However, using an actual dyeing has the important advantage that it is mill-specific.

In the event that the dye is used on blends, be sure to use the blend procedure. For example, a disperse dye which is normally used on polyester/cotton blends, for disperse/direct one-bath dyeing, should be dyed with salt and other direct dye auxiliaries. Care must be taken to have a consistent supply of substrate for use on a long term basis for such dyeings.

Another quick and simple test is chromatography. Selected developers for thinlayer chromatographs of various dye classes are given in Table VI, and for paper chromatography in Table VII. Another application of the paper chromatography technique is in the drug room. When each dye recipe is pasted up for use, a few drops of dye mix are spotted on a piece of filter paper. If a problem is later detected, the spotted paper can be eluted to determine qualitatively that the correct dyes were in the mix. If printing scales were used for weighing, the amounts of each dye weighed can be verified also. Alternative solvents for development of chromatograms are given in Table VIII.

One of the most important aspects of testing of dyestuffs is to review all test data, good or bad, with the vendor. This establishes communications before problems arise, and also makes the vendor aware that the mill is checking. (Vendors also ask the question "Who is the customer?").

Standard test methods

There are many standard test methods that pertain to troubleshooting in dyeing. These are listed in Table IX. The applicability of these tests to various situations in exhaust and continuous dyeing will be described in detail in Parts II and III of this article. ☐☐☐

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Troubleshooting In Dyeing—
Part II: Batch Dyeing

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Abstract

The first part of this article (Mar. 87 ADR) presented some fundamental aspects of dyeing quality control in general. This part (II) presents specific details of controlling batch dye processes. Critical quality control parameters are discussed for various dye classes, equipment, processes, and substrates. Also, diagnostic tests and repair procedures are presented. The final part of this article will concentrate on continuous dyeing.

Introduction

Many different classes of dyes are applied to various substrates by batch methods in mill-specific situations using a wide variety of equipment. It would be impossible to review each and every commercially important combination of circumstances in depth; therefore, information presented herein is intended primarily as a guide for troubleshooting in a variety of bath dyeing production situations.

Dyeing defects

Various types of defects may occur during batch dyeing and particular combinations of processes, equipment, dyes or substrates may be more or less susceptible to specific types of defects. Most production dyers cite various defects, such as those listed in Table I, as their major problem areas. However, there is no question that the major problem which occurs in batch dyeing is poor shade repeats (off shade dyeings).

In addition to production which gets out of the dyehouse with an unacceptable shade, poor shade repeats actually are the underlying cause of a substantial portion of physical damages, uneven dyeings, and foreign deposits. These defects frequently occur when a shade does not repeat properly and requires corrective action such as dye or chemical adds, extra run time, boiling down, stripping, redyeing, and/or overdyeing. Corrective/repair procedures require extra time and processing; hence, the risk of physical damage is greater. Practices such as stripping or adds increase the risk of uneven dyeing and bath instability.

Consideration of dyeing economics and losses associated with dyeing defects must take into account the relative value of the substrate (frequently several dollars per pound), versus the actual labor, overhead, dye, and chemical cost for dyeing (usually less than $0.50 per pound for most shades). Thus, a relatively large savings in dye cost can be quickly offset by even a minor increase in defect level and the associated losses such as the loss of expensive substrate. For example, a 10% cost reduction on a dye cost of $0.25 per pound would be offset by an increase of only 1% off-quality on a $2.50 substrate.

In addition, that 1% off quality might be reworked or redyed by a costly procedure (causing additional economic loss) which has a higher risk and lower chance to produce acceptable product than first-run dyeings. Thus the dyer's priority must be to avoid producing defects. To avoid defects, the first step must be to produce consistent shade repeats.

There is a very widespread impression that avoiding defects, and especially improving shade repeats, is a simple matter of discipline. Although supervision, good maintenance, and proper operation of equipment are important, it is also very important to put quality (not cost reduction and short cuts) as the number one priority. Management pressure to reduce cost or increase production beyond reasonable limits (for example, by overloading equipment) is frequently counterproductive.

Dye selection

The exhaust dyer has a wide variety of colorants from which to select his dye recipe. Many considerations enter into selection of dye class, subclass, and specific dyestuffs. A typical selection protocol is shown in Table II. Sometimes special situations such as unusual blend, substrates, constructions, or production volume arise which require complete review of the entire formulation protocol. In these cases, it is important to make a careful evaluation and not to treat the situation as "routine." To avoid trouble, these situations must be identified in advance and handled properly in terms of equipment, process and dye selection, quality control requirements, cost analysis, and expectations for off-quality and re-working. Using a certain set of dyes, procedures, cost analysis, etc., from habit is sure to lead, sooner or later, to trouble.

Examples of such situations are not difficult to find. One example which frequently occurs is the design of difficult-to-dye blends, especially three fiber blends, by stylists who do not realize the difficulties involved. The dyeing behavior of many binary

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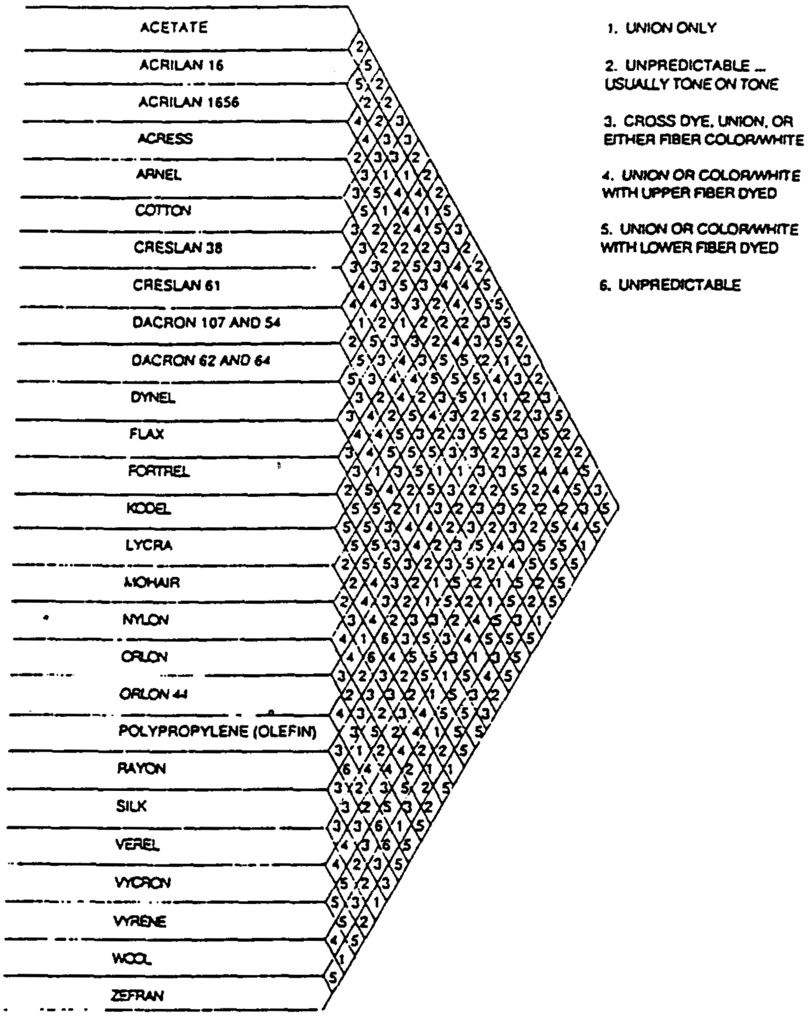
Editor's Notes—Third in a series of ten articles to be prepared by Dr. Brent Smith on the general theme, "Troubleshooting In Wet Processing".

Figure 1: Fiber Dyeing Chart



blends is given in Figure 1 (the original source of this widely circulated table is uncertain). Introducing a third fiber can create great difficulties for the dyer.

One specific commercial example of such a situation involved a polyester/cotton/acetate blend. The idea of the designer was to make a two-sided fabric with filament acetate yarn on the face and a spun yarn on the back. Although the back side of the fabric could have been made from 100% cotton yarn, the designer selected 50/50 polyester/cotton yarn by habit. The resulting three-fiber blend (polyester/cotton/acetate) was a dyer's nightmare in dark shades because of difficulties in disperse dye selection as well as the physical and chemical damage which occurred to the acetate while dyeing the polyester and cotton. An alternative fabric, with filament acetate yarn on the face and 100% cotton yarn on the back, on the other hand, was relatively easy and less costly to dye.

The two important ideas in this example are to design products which have the greatest potential for overall profit and when high degree-of-difficulty products are encountered, to have special procedures for handling them.

In exhaust dyeing, proper selection of a specific dye combination for a shade is critical. Factors such as exhaust rate (strike), leveling properties, and sensitivity to pH and electrolyte must be consistent for all dyes in the formula. AATCC Test Methods 141 and 156 for basic dyes, 155 for disperse dyes, and 159 for acid dyes are helpful.[1] Exhaust curves prepared by instrumental color analysis of the dyebath or the substrate are also helpful. Exhaust rate compatibility can also be evaluated by private methods such as the Resolin S Process.®[2] Failure to select compatible dyes in combination shades will affect shade repeats.

Suggestions for quality control of dyestuffs for a dyehouse are given in Part I of this article. Storage, weighing, and mixing of dyes should be in a cool dry area. Proper ventilation and air circulation are important for worker protection and also to prevent airborne dye particles from flying or drifting to areas where they might deposit on in-process goods. Certain dyes, especially fiber-reactive powder dyes and many types of liquid dyes, have a tendency to degrade during storage. All drums of dye (and also chemicals) should be dated when opened. Any drums which are nearing the end of their shelf life, as recommended by the manufacturer, should be retested using standard raw material quality-control procedures.

Paste-up of dyes can have a substantial effect on the quality in terms of shade repeats as well as specific defects such as dye spots. Therefore, dye paste-up should adhere carefully to manufacturers recommendations. General guidelines for drug room practices given in Table III are not intended to contradict or substitute for specific instructions which a dye manufacturer might provide for a certain dye. Beyond these specific procedures and temperatures, however, there are other considerations.

When dyes are weighed, it is an advantage to use printing scales for a permanent record of amounts, and to dip the corner of a piece of filter paper in the final paste for diagnostic chromatography test later, if necessary.

If the water is hard, hexaphos should be added and thoroughly dissolved prior to pasting dye.

If chlorine is present in the water, 1 gram per liter of thiosulfate should be added. Excessive amounts of thiosulfate are detrimental.

Sequestrants for iron and copper (EDTA, DTPA, NTA) should not be used because many dyes are sensitive. If metals such as iron and copper are a problem, water treatment (not chelates) should be employed.

Some paste-up procedures given in Table III mention the use of live

Table I: Batch Dyeing Defects

— *Physical damage:*
- tender or weak,
- scuffed, pilled, chafed or abraded fabric
- frayed or abraded yarn
- picked or snagged fabric
- holes, torn, or broken fabric or yarn,
- creases, cracks, breaklines, or rope marks in fabric

— *Uneven dye application:*
- streaky fabric or yarn,
- shaded goods (side/side, end/end, inside/outside, etc.),
- blotchy.

— *Foreign deposits:*
- dye spots,
- wax, oil, or size spots,
- chemical breakout (bath instability),
- filtering deposits.

Table II: Formulation of Dye Recipes

1. *Select Equipment:*
   - Production Volume Expected
   - Cost Requirement (Market Competition)
   - Physical Form of Substrate
   - Quality (Reproducibility vs. Evenness)
   - Availability of Equipment
2. *Select Dye Class:*
   - Substrate (Fiber Content, Blend)
   - Equipment/Procedure
   - Cost Requirement
   - Fastness Requirement
3. *Select Specific Dyes (within Class):*
   - Safety/Environmental
   - Availability
   - Cost
   - Fiber Content of Substrate (esp. Blends)
   - Fastness
   - Shade Reproducibility and Evenness Required
   - Quality Factors (Fastness)
   - Value, Chroma, Hue of Colorants
4. *Match the Color:*
   - Percentages of Dyes/Chemicals to Use

steam, which is common practice in some drug rooms. If live steam is used, there is a risk of introducing metal contamination from the steam pipes. Also, using live steam can raise the pH of the heated water due to alkaline contaminants in the steam. It is not unusual to find pH values of 8.5 to 9 or higher for water which has been heated to 180°F with live steam. If live steam is used, check frequently to ensure that metallic contamination and alkalinity are not being inadvertently introduced into dye pastes, dyebaths, and washing/scouring operations.

Various dye classes exhibit substantially *different* behaviors in thermo-dynamic equilibrium (isotherm) and kinetics (exhaust or strike).[3] To be successful, dyeing procedures and equipment must be compatible with these behaviors. Of course, individual dyes within a class may have *substantial* variations which must be considered. Excellent presentations of the fundamentals of exhaust dye applications have been published.[4] For each dye class, there are certain critical factors to be controlled or special considerations to be made in order to avoid trouble.

One particular factor is the manner of determining amounts of chemicals to be used in exhaust dyeings. The dye, of course, must be based on the weight of fiber to be dyed. It is common practice to base amounts of chemical auxiliaries also on the weight of fabric. This can create problems with shade repeats, for example when acid, alkali, or other buffers are used to adjust pH to specific values or when electrolyte is used. Therefore, quantities of these chemicals should be based on the amount of dye liquor present. Failure to do so is a prominent cause of poor laboratory-to-dyehouse correlation, as well as poor shade repeats on odd-sized lots. When liquor ratios vary, basing chemicals on the amount of goods causes variations in concentrations which in turn changes the percent exhaust of dye, therefore affecting shade repeats. Typical laboratory liquor ratios will usually be over 20:1, while typical production liquor ratios will be 8:1 up to 16:1.

Even when chemicals are based on the bath, changing liquor ratios can cause shade variations. To adjust dye recipes for variance in liquor ratio requires knowledge of the dyeing behaviors described in Part I of this article. In particular, the effective value of "K" in the isotherm (at equilibrium) must be known for the dyeing.

$$K_{eff} = [D_f] / [D_s]$$

The liquor ratio L and K_{eff} are related to the equilibrium exhaust E by equations 2 and 3.

$$E_\infty = K_{eff} / [K_{eff} + L]$$

or

$$K_{eff} = [E_\infty L] / [1 - E_\infty]$$

A laboratory dyeing which had 90% exhaustion at equilibrium determined by colorimetric measurements of residual dye in the dyebath, and a liquor ratio of 25:1 would have:

$$K_{eff} = (0.90 \times 20) / (1.00 - 0.90) = 180$$

When the same shade is dyed on production machines at 10:1 liquor ratio, a value of exhaustion of:

$$E_\infty = 180 / (180 + 10) = .947 \text{ or } 94.7\%$$

Thus to get 1% ye on the goods in the laboratory (25:1 liquor ratio) requires 1.11% dye *on weight of goods* (owg), but in the production machine (10:1 liquor ratio) requires 1.06% dye owg. Failure to make an appropriate adjustment would result in poor laboratory-to-dyehouse correlation, even if chemicals were based on the dyebath.

Another source of variations in dye exhaust is the substitution of Glauber's (GL) salt for common salt. Several dye classes use salt to achieve exhaust, and several types of salt can be used, including;

- — Common salt ($NaCl$)
- — GL salt heptahydrate ($Na_2SO_4 . 7H_2O$)
- — GL salt anhydrous (Na_2SO_4)
- — Brine ($NaCl_{aq}$)

Because of the differences of formula weight between the above, substitution should *not* be made on equal pound-for-pound basis. Actual equivalences are:

100# Common salt
122# GL salt anhydrous
278# GL salt heptahydrate
38.5 gallons brine
(23 Be or 25% NaCl)

Dye adds

One common practice in exhaust dyeing is the addition of dyestuffs (adds) to an exhausted bath in order to adjust a shade which did not properly repeat. The manner in which such adds are made can substantially affect overall dyehouse performance. Making adds to production dyeings is difficult at best. The main difficulty which arises is that something, often unknown, has caused the shade to fail to repeat. It could be pH, salt content, contamination in raw water, inaccurate weighing of dyes or chemicals, poor temperature control, leaking drain or fill valve, improper dye or chemical addition procedure, variations in substrate preparation, etc. In many cases, excess dye is still in the bath and is not exhausted onto the fiber. Therefore, nonstandard-dye exhaustion has occurred, and the proper first action is to correct the dyeing as nearly as possible to standard conditions.

If the problem is procedural in nature, such as an error in time, temperature, pH, salt content or liquor ratio, there is little chance that a dye add will behave any better than the original dyeing. To allow for this, dyers have learned to "hedge" their adds in order not to overshoot. In fact, it is rare for a dyer to make a large add to correct a shade in one try; multiple adds are common. This greatly increases the risk of streaky or damaged goods. To make a good dye add requires careful judgment of the exact reason for the failure of the shade to repeat, inspection of the dyebath for unexhausted dye, determination of pH and electrolyte content, and determination of whether a dye (color) add is the correct action. Some things that can be done to make adds easier for the dyer are to establish:

- Good shade repeats in the lab, and good lab-to-dyehouse correlations;
- a reproducible production dye recipe and procedure for the shade;
- a dyer's take-off shade guide, produced from the same recipe on the same substrate (not finished) for color difference determinations, shade passing, and estimating dye adds; and,
- to inspect the dyebath for dye, pH, salt content and other factors before adding color.

Other factors for controlling shade repeats and even dyeings are presented below for specific dye classes.

Acid dyes

Acid dyes obey the Langmuir isotherm when applied to wool and nylon, and undergo strong ionic interaction. Acid dyes, as a class, are relatively easy to apply. It is important to select dyes with compatible exhaust characteristic and appropriate properties with regard to end uses. Exhaust and leveling are controlled by pH. Traditionally ammonium sulfate has been used to generate acid in the bath when ammonia is released by the reaction:

$$(NH_4)_2(aq)\ SO_4(aq)\ 2NH_{3(g)} + H_2\,SO_{4(aq)}$$

This does not work well for pH control on modern enclosed dyeing machines such as jets, beams, package dye machines, and pressure becks because the enclosure of the machine prevents the ammonia from escaping. On such equipment, alternate buffer systems should be used.

If an acid such as formic or acetic is used for pH control, addition should be even and slow. Lightfastness of acid-dye recipes, which is generally very good, can be improved even further by the addition of copper sulfate to the dye bath. However, copper-containing baths must be handled by special techniques, such as reuse, to avoid environmental or waste treatment problems.

Repair procedures for acid dyes include leveling by boiling (ph must be controlled in accordance with the specific dye selection), or stripping. Stripping procedures include reduction (zinc sulfoxylate/formaldehyde), oxidation (sodium chlorite), or specially ethylene-oxide-tallow-amine stripping agents which have affinity for the acid dye and complex it in solution. The specialty strippers work at slightly alkaline pH, provided by adding TSPP to the bath. Lightfastness of stripped and redyed goods is frequently inferior to first-run goods.

Basic dyes

Basic dyes obey the Langmuir isotherm when applied to acrylics, and undergo strong, ionic interaction. Because of the strong affinity of basic dyes for acrylic (and other basic-dyeable) fibers, exhaust is nearly 100% and migration or leveling is generally poor. Therefore, the selection of dyes with similar exhaust characteristics is of primary importance. There are several methods for determining compatibility, including AATCC Test Method 141. Other methods such as "diffusion numbers"[5] and affinity determinations[6] can also be used. Careful attention to dye compatibility is necessary to obtain consistent shade repeats, on-tone shade build up, and even dyeing.

The dye process itself must be properly designed. Because acrylic fibers have a relatively sharp glass transition (T_g) temperature and because of the strong affinity of basic dyes to anionic dye sites in the fiber, exhaust (strike) begins very rapidly at a specific temperature. Also, fabrics which are run in rope form tend to form permanent creases if heated or cooled rapidly in the temperature range near T_g. Therefore, it is best to be very conservative with heating and cooling near T_g.

Typical T_g values for acrylics are in the range of 175° to 190°F, but the T_g of wet fiber under tension in the dye bath may be significantly different from the dry T_g reported by the fiber manufacturers. To repair creases and cracks in acrylic fabrics, heat 210° to 225°F, run 15 minutes, then cool back to well below T_g very slowly (0.5°F/minute).

Retarders are frequently used to assist in even shade buildup. Glauber's (GL) salt acts as a mild retarder. Specialty retarders have stronger effects such as permanently blocking dye sites or complexing dye in the dye liquor. It is possible to make a retarder with precisely controlled action by mixing GL salt with various specialty retarders. Also, GL salt will help prevent degradation of some basic-dyeable fibers at temperatures of 210°-225°F. Basic dye carriers, used for copolymer polyesters, can help reduce stain on other fibers in blends, and can improve lightfastness in blends.

Chlorine and iron contamination in water cause poor shade repeats and uneven dyeings.

Stripping of basic dyes can usually be done easily with hypochlorite at a pH of 4 and 210°F. However, it is important to be sure that all traces of chlorine have been removed before redyeing, otherwise poor shade repeats will result. To reduce or pull down the shade, the goods can be boiled off with high concentrations (8%) of naphthalene sulfonic acid or treated with 2% to 4% benzyltrimethyl ammonium chloride (BTMAC) at a pH of 4 for 1 hour at 230°F. On package dye or beams, run BTMAC boil-off I/O (inside/outside) only for best results.

Direct dyes

Direct dyes obey the Freundlich

isotherm, when applied to cellulose, and undergo weak interaction with the fiber. There are three subclasses or types of direct dyes. Type A directs have good migration and leveling properties even in the presence of salt. Type B directs level well without salt, but not so well when salt is present. For this reason, salt addition must be very carefully controlled, especially if brine is used. However, penetration and leveling may be achieved with type B directs by boiling the dyebath prior to salt addition. Type C directs do not level well at all, and evenness of exhaust must therefore be assured by careful temperature control. Type C are relatively very difficult to dye, and exhaust must be controlled by careful heating. Details of dye processes for directs such as addition of salt (hot or cold) and rate of rise must be carefully tailored to the dye types in the recipe.

Important factors in dye selection for directs include type compatibility, exhaust temperature compatibility, dead cotton coverage, fastness, and blend considerations (staining). Maximum exhaust temperature for individual direct dyes varies. Examples of a few direct dyes and their maximum exhaust temperatures are shown in Table IV. The practical implications of these temperatures of maximum exhaust are important.

Suppose a recipe had for example CI Directs Red 81, Blue 80, and Yellow 105, which give maximum exhausts at 140°F, 205°F, and 203°F, respectively. If the dyeing were done at 205°F, the Red 81 would continue to exhaust during the cooling part of the dye cycle. Thus the fabric sample ("hot patch") taken at the dyeing temperature of 205°F would not contain as much Red 81 as the final (cold) patch. This may lead to poor shade repeats or even worse, unnecessary dye adds based on an inaccurate hot patch.

When direct dyes are used for blends, several special considerations must be taken into account. One important consideration is the selection of dyes with good stability at high temperature. This is very important when dyeing synthetic/cellulose blends together in the same bath above 212°F. High temperature stability of some dyes is given in Table V. Many direct dyes are hydrolyzed by slightly-acidic conditions at extended times and high temperatures (250°F.) These dyes must be avoided if good shade repeats are to be obtained.

Direct dyeings have inadequate fastness for many end uses unless some sort of fixative is applied. Several types are commonly used to improve wet fastness of direct-dyed goods. The misuse of fixatives is frequently a contributing factor to off-quality direct dyeings. The use of copper sulfate has been largely discontinued because of its detrimental effects on the environment. Epsom salt is sometimes used as an antimigrant to temporarily fix the dye until a permanent fixative can be applied from a continuous finish mix.

More commonly, resinous fixatives are either exhausted from the dyebath or applied in finishing. Improper application of these resinous fixatives can cause spots and streaky, blotchy, or shaded dyeings. The first point of concern is never to introduce the fixative into a direct-dye bath which is not clear of dye. If any dye remains in the bath, adding fixative will immediately precipitate it, thereby producing defective goods. To clear the bath, many dyers use salt in the final rinse. However, many fixatives will precipitate in the presence of salt, giving resinous spots. To avoid fixative spots or streaks, take the following precautions:

- never add fixative hot; keep temperature around 80° to 100°F while adding fixative;
- be sure the bath is clear of dye before adding the fixative;
- if washing in salt, be sure that the fixative is compatible with salt;
- heat the dye bath to 140° to ensure fixative exhaustion, using a slow, even rate of temperature rise;
- watch out for chlorine hardness, iron, etc. in the water during the fixing processing, (add thiosulfate and/or hexaphos if necessary); and
- keep control of the pH according to values recommended by the fixative manufacturer (typically about 4).

Direct dyes are commonly applied with salt and the amount, type, and manner of addition of salt is important to ensure reproducible and level dyeings. The total amount should be 10 grams per liter of common salt for each 1% of direct dye in the recipe. However, the total amount of common salt should not be less than 5 grams per liter nor more than 40 grams per liter. The amounts should be based on the bath (not the goods) and amounts should be properly adjusted if GL salt is used instead of common salt, as discussed previously.

The amount of electrolyte actually in a bath can be determined by techniques such as conductivity measurement, which can easily be done with a pH meter equipped with a conductivity probe.

Salt must be added evenly and slowly, preferably in 3 to 5 parts. Great care must be exercised when adding brine due to its extremely fast action on the dyebath. A good scheme for fractions in a four-part salt addition are:

1/8 : 1/8 : 1/4 : 1/2;

allowing 10 minutes between each salt addition This is most critical for type B and C.

Some other critical factors to be considered:

- Watch the pH
  7 to 9 for 100% cellulosic fabrics (all direct)
  6 to 6.5 for direct/disperse (blends)
  4.5 to 6 for direct/basic (blends);
- Metals and sequestrants interfere with many directs,

Table III: Dye Paste Up Practices

Add 1 gram per liter thiosulfate if chlorine is present in the water.
Add hexaphos if hardness is present in the water.
Do not use EDTA, DTPA, NTA, or similar sequesterants.
Be careful when using live steam (pH and metal contamination).

Direct Dyes
Mix dye directly into cool (80°F) water
With stirring, heat (live steam is OK) to 160°F
Continue stirring until used

Basic Dyes
Paste dye in equal weight of acetic acid
Add dye paste to 200°F water with stirring
Avoid live steam (even before adding dye)

Acid dyes
Add dye directly to water with stirring
. . . premets, cool (80°F)
. . . leveling types, hot (180°F)

Fiber Reactive Dyes
Add dye directly to water at 140°F to 170°*F with stirring*
Avoid live steam (even before adding dye)
Add 10 grams per liter or more of urea to increase solubility
If solubility problems persist, use liquid dyes.

Disperse Dyes
Add dye to 110° to 115°F water, with stirring
Avoid live steam (even before dye is added)

Vat, Sulfur, Naphthol, Developed, Mordant dyes
Follow manufacturer's instructions (varies)
These are usually available as liquids

Table IV: Temperature of Maximum Exhaust for Selected Direct Dyes

CI Direct	*Temp. (°F)*	*CI Direct*	*Temp. (°F)*
Yellow 50	140	Blue 1	140
Yellow 106	203		
Yellow 105	203	Blue 80	205
Orange 39	175	Blue 218	203
Red 81	140	Black 80	212
Violet 4	158	Black 22	212

Table V : Stability of Direct Dyes @ 250°F, pH 6

Direct Dyes with Good Stability @ 250°F, pH 6

Shade	*CI Number (Direct)*
Yellow	8, 11, 12, 27, 28, 29, 98, 105, 106, 114, 127, 137
Orange	34, 37, 57, 107
Red	2, 9, 16, 76, 81, 89, 207
Violet	49, 51
Blue	2, 71, 76, 77, 80, 86, 90, 98, 160, 191, 218, 224
Green	26, 29, 31, 33
Brown	2, 95, 113, 200
Black	38, 51, 78, 80, 91

Direct Dyes with Poor Stability @ 250°F, pH 6

Shade	*CI Number (Direct)*
Yellow	34, 39, 44, 50, 84, 107, 110, 119, 131
Orange	29, 39, 72, 78, 80, 91
Red	1, 24, 62, 72, 75, 79, 80, 83, 95, 212, 236
Blue	106
Violet	66

especially at high temperature (250°F for polyester/cotton blends).
- Dyebath assistants such as lubricants or carriers, levelers (for blends) can retard dye exhaust and/or affect shade repeats, staining, fastness, etc.

Repair of direct dyeings can be done only after removal of any fixative and/or resin finish from the goods. A quick test with carbozole can detect the presence of finish. After finish removal, dye can be leveled by raising the pH to 8-9 with soda ash, boiling down the shade, and then salting back. Stripping can be done with either hydro/soda ash or hypochlorite depending on the specific dye recipe. Some dyes, such as CI Direct Yellow 105 cannot be stripped satisfactorily.

Disperse dyes

Disperse dyes interact weakly and form solid solutions of dye in synthetic substrates and follow the Nernst isotherm. Because goods are dyed above T_g of the fiber, there is a risk of shrinkage, moire, permanent creases, cracks, or rope marks, especially if heating and cooling are rapid. A combination of several factors must be considered to ensure compatibility of the dye recipe, chemical auxiliaries, substrate machinery, and process. These factors can be quantified by any of several commercial methods[2,5] which take into account:

- dyeing speed of fiber;
- time/temperature of procedure
- dyestuff characteristics (subclass);
- accelerant (carrier) used; and,
- machine turnover/rate of heating.

As with other classes, rate compatibility of all dyes in a recipe is essential for good shade repeats.

Another important factor in dye selection is the ability of dyes to level. Dyes with good leveling properties can be exhausted more rapidly with less chance of streaking the goods. The ability of dyes to level can be determined by several methods, including AATCC Test Method #155 or "transfer index". Leveling ability of several dyes in typical production processes is shown in Table VI. Dyes with high values (above 30) level well, dyes with lower values (less than 20) do not level as well.

Table VI: Leveling Ability of Disperse Dyes
[Transfer Index (TI); 50 = Best, 0 = Worst]

Dye CI Disperse:	*TI*	*Dye CI Disperse*	*TI*	*Dye CI Disperse*	*TI*
Yellow 54	50	Blue 60	32	Orange 41	15
Yellow 67	36	Blue 56	35	Brown 2	24
Orange 25	32	Yellow 93	34	Violet 26	20
Orange 44	32	Red 55	25	Blue 27	18
Red 11	33	Red 59	30	Yellow 42	5
Red 60	36	Red 65	25	Orange 21	4
Violet 18	33	Yellow 23	16	Red 135	2
Violet 27	33				

Transfer index is determined by placing a dyed fabric and a mock-dyed (white) fabric together in a mock-dye bath. Color transfer is measured as:

$\text{Dye desorbed} = [(K/S_{before} - (K/S_{after}] / (K/S_{before}$

$\text{Dye absorbed} = (K/S)_{transfer} / (K/S)_{after}$

$\text{Transfer index} = [\text{Dye desorbed}] \times [\text{Dye absorbed}] \times 100$

where:
$(K/S)_{before}$ = color value of dyed cloth prior to leveling;
$(K/S)_{after}$ = color value of dyed cloth after leveling; and,
$(K/S)_{transfer}$ = color value of white cloth after leveling

Many dyes, such as CI Disperse Yellow 42, appear to be bargains in terms of color value for the price, but they can present significant leveling problems with certain types of exhaust-dyeing equipment and processes.

Some machines, especially those which pump the dye liquor, such as jets, beams and packages, can have problems in specific temperature ranges due to cloudpoint effects of nonionic emulsifier and surfactant systems used in many chemical specialties. This can cause spots, poor crocking fastness, and other problems.

Other commonly encountered causes of defects in exhaust dyeing of disperse dyes include filtering of dye in package machines and beams, metal sensitivity and oil spotting, poor wash and crocking fastness, and dulling of shade by salt (usually for dyeing blends). Filtering and bath stability can be evaluated by AATCC Test Method 146. The effect of metal contamination in process water is reviewed in another article in this series, Water and Textiles Wet Processing—Part II.[7]

Oil spotting, the development of dye spots due to oil (especially knitting oil) on goods, is especially a problem with colorants such as CI Disperse Red 60. Spots may also appear when dyebath contaminants, especially fiber finish, polyester size, and/or trimer, precipitate as the dyebath is cooled. This can be avoided by the use of dyebath auxiliaries (dispersants/surfactants), or dropping the bath hot (above 190°F)

Disperse dyes are difficult to strip, especially from polyester. Useful procedures are excess carrier with either reducing agents (hydro/caustic) or chlorite (Texton®). Sometimes a sequential strip with hydro/caustic followed by chlorite at 250°F is effective.

Disperse/direct blends

When dyeing polyester/cotton blends with disperse/direct dye recipes, some important factors must be considered in addition to those presented above for pure substrates:

- disperse-dye leveling agents and carriers can affect direct shade repeats and leveling properties;
- disperse-dye carrier can influence direct-dye stain on polyester, giving poor fastness;
- keeping the pH near 6 is a good compromise for both dye classes;
- disperse dye leveling agents and carriers may be sensitive to salt, especially under conditions of high shear (pumping) or at specific temperatures;

- sequestering agents of the EDTA, NTA, or DTPA type may influence shade repeats of direct and disperse dyes; and,
- lubricants are sometimes necessary and appropriate, but they may influence shade repeats and evenness. Also lubricants may have incompatibility with salt or high temperatures.

Fiber reactive dyes

The application of fiber reactive dyes has a fairly high degree of difficulty compared to other classes. Perhaps one reason for this is the large number of choices to be made concerning dye type (hot vs. cold), procedure (conventional, constant temperature, high temperature, or all-in), and alkali (bicarb, soda ash, TSP, silicate, or caustic). Also, the importance of procedures after dye application, especially washing off and fixing, are frequently overlooked. Fiber reactives in general are more adversely influenced by variations in cotton, poor preparation, "dead" or immature cotton, neps, and other substrate differences than are other cellulosic-dye systems. Also, making dye adds to reactive dyeings is far more likely to cause a defective dyeing than are other classes, such as directs.

The hot-dyeing types are less reactive, therefore, require higher temperatures. They are more stable to hydrolysis and precise temperature control is not as critical as for the cold-dyeing types. Also, penetration of the dye and leveling is better with the hot-dyeing types.

Dye cycles are usually shorter with the cold-dyeing types, leading to less "working" of the goods. This can either be good or bad, depending on the specific situation, the hand desired, ruggedness of the goods, etc. The cold types are especially sensitive to variation in heating rate or reaction temperature control, therefore they are extremely difficult to run consistently on equipment with poor temperature controls or in mills with inadequate boiler capacity to supply peak steam demands.

Table VII: Fiber Reactive Dyeing Methods

	Conventional	*Constant temperature*	*High temperature*	*All-In*
1.	Set bath and load substrate	Set bath and load substrate	Set bath and load substrate	Set bath and load substrate
2.	Add dye	Add dye	Add dye	Add dye
3.	Run	Run	Run	Run
4.	Add salt	Heat to dyeing temperature*	Heat to high temperature*	Add salt
5.	Heat to dyeing temperature (*)	Add salt	Cool to dyeing temperature *	Heat to dyeing temperature*
6.	Add alkali	Run for exhaust	Add salt	Run for exhaust and reaction
7.	Run for reaction	Add alkali	Run for exhaust	Cool
8.	Cool	Run for reaction	Add alkali	Wash
9.	Wash	Cool	Run for fixation	Apply fixative
10.	Apply fixative	Wash	Cool	—
11.	—	Apply fixative	Wash	—
12.	—	—	Apply fixative	—

*Typical dyeing temperatures are 175°F for hot types, 140°F for cold

**High temperatures are 203°F for hot types, 160° for cold

The hot-dyeing types are usually harder to wash off, therefore the washing required after dyeing is more critical.

Cold dyeing types show more of latent defects from preparation. Of course, less energy, salt and alkali are required for the cold-dyeing types, but without excellent temperature control, these savings are quickly offset by quality losses.

Each fiber reactive dye has distinctive characteristics which influence how it will behave in a particular process. These include substantivity and reactivity. Figure 2 shows the effect of these two factors upon dye exhaustion. Unlike direct dyes, some fiber reactive dyes do not fully exhaust until alkali is added. Thus the manner of addition of alkali is even more critical than addition of salt due to the rapid exhaust that occurs upon the addition of alkali as well as the fact that the reactive dye will not level appreciably after alkali addition. The four methods most widely used in commercial dyeing operations for fiber reactive dyes are summarized in Table VII.

The conventional procedure gives good shade repeats and is fairly simple to run. Penetration and leveling are better than the all-in method but not as good as the high-temperature method. Good temperature control is essential.

The constant temperature method is simple to run and is the most forgiving in terms of temperature fluctuations. Leveling and penetration are better than all-in but not as good as the high temperature method.

The high-temperature method is more complex, longer to run, and consumes more energy, however it gives the best penetration and leveling, and is especially useful on problem styles or poorly prepared goods. The goods are subjected to more physical "work" also; thus the handle of the fabric is affected and physical damage (pilling, or abrasion) is more likely. Shades generally do not repeat as well when this method is used, however it is not certain whether this poor repeatability is due to the method itself or due to the generally poorer preparation of goods for which this procedure is designed.

The all-in method is the simplest, shortest and least expensive to run

Table VIII: True-Shade Beck Capacities

(Gallons per beck foot)

Liquor Depth (inches)	Model 85				Model 850		
	Type O	Type P	Type R	Type S	Type O	Type P	Type S
18	52	60	65	75	47	60	70
21	64	74	80	91	58	72	85
24	76	88	95	108	70	85	101
27	89	102	110	125	81	98	117
30	102	116	125	142	93	110	133
33	114	129	140	158	105	123	149
36	127	143	155	175	116	136	165
39	139	157	170	191	128	149	182
42	152	171	186	208	140	162	198
45	164	185	201	224			214
48	177	199	216	241			
51	189	212	231	258			
54	202	226	247	275			
57	215	240	262	291			
60	228	254	277	308			

Model 85 has straight front - Model 850 has curved front
Front to back dimension
Type O = 7'2", Type P = 7 '11", Type R = 8'8", Type S = 9'5"

in terms of labor, steam, and other factors. Because the dye is exhausting, fixing, and hydrolyzing all at the same time in this method, shade repeats are poor, dyeings tend to become uneven and streaky unless the temperature control is almost perfect. Turnover times for the bath and/or fabric must be adequate to insure even exhaustion of the dye, as no leveling will occur. This method is extremely risky, overall, especially with the cold-dyeing types which react and hydrolyze so rapidly.

Reactive dyes are sensitive to alkalinity, chlorine, residual peroxide, and metals. Good water treatment and well-prepared goods are essential. Thorough washing off of unreacted dye is important to get good shade repeats and level dyeings. On machines with poor washing efficiency, such as beams, jigs and package-dye machines, fixative should be used to prevent migration of dye. More washing is needed when using stronger alkali, such as caustic soda. Some dyers use potassium hydroxide (instead of caustic) since it washes off easier. Fixative handling procedures should be the same as discussed under direct dyes.

Use of hydro/caustic or hypochlorite will generally result in a complete stripping of reactive color. However, dye sites on the cellulose may remain blocked due to residual fragments of dye. Therefore, redyeing of stripped goods will behave differently than dyeing of new goods. In particular, more alkali and time may be required.

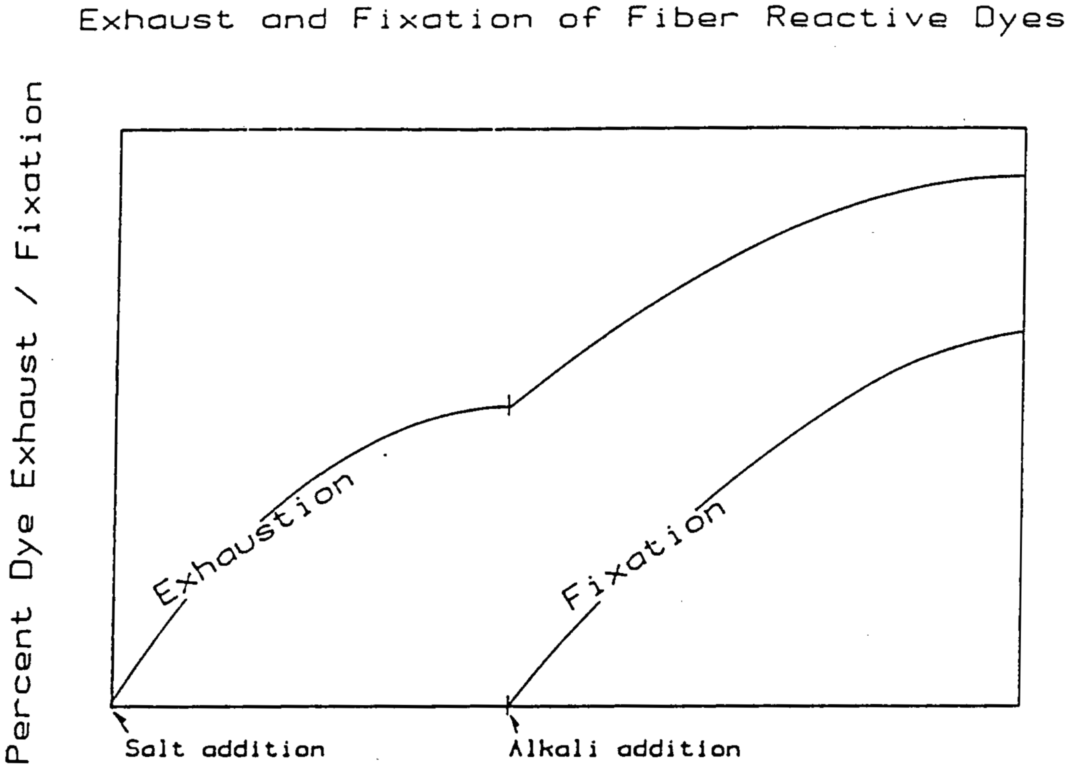
Equipment

Many different types of equipment are used for exhaust dyeing. Some good general guidelines for various equipment is given below.

Becks are one of the oldest traditional types of equipment for exhaust dyeing. Their continued popularity indicates the versatility and economy of becks. They provide quite a lot of mechanical action to the fabric. Older models, which generally lack heat exchangers and circulating pumps, frequently have problems with temperature differentials (front-to-back, end-to-end) as well as the difficulties associated with the use of live steam. These machines cannot be properly heated unless they contain cloth. Therefore, any attempt to heat prior to loading the fabric is futile.

Since the electrolyte and alkali are to be used on the basis of bath volume, it is important to know the exact amount of dye liquor in the beck. This can be determined either with a water meter or by the use of commonly available tables like Table VIII. An audit checklist for mechanical condition of becks is presented in Table IX. An operations checklist for becks is shown in Table X. Careful attention to these details through

Figure 2



preventive maintenance and good supervision will pay dividends in quality. Pressure becks have a few additional points of concern, primarily pressure leaks which cause boiling and tangles.

Equipment factors

Modern package and beam-dyeing equipment have extremely high bath turnover. Because of this, bath stability is critical. Instability of the dyebath due to shearing action of high speed pumps, high temperature or rate of rise, short liquor ratio, cloudpoint, or chemical incompatibility will lead to filtering and deposits. Because of the higher flow rates, winding is more critical for new machines than for older, lower-flow machines. Acceptable flow rates are in the range of 3 to 5 gallons/minute per pound of load. Filtering problems usually can be traced to water (sediments, alum, hardness), trimer or fiber finish, or bath instability (shear, temperature, cloudpoint or chemical compatibility). Substrate contaminants such as metals, trimer, waxes and oils, residual bleach or alkali can create problems. Drying of package-dyed yarn should be done promptly within 4 to 6 hours to avoid migration of dye. A good extraction ("blow-down") cycle will save energy as well as reduce dye migration. Fixatives can be used on fiber reactives to minimize migration.

Beam-dyeing machines have many features similar to package dyeing machines. Batching is critical, and should begin with eight or more layers of lapping cloth to avoid perforation marks. Uniform batching prevents shade variations within the load and should be done with moderate tension. If tension is too high, moire, low flow or blown beams will result; if too low, channeling and uneven dyeing will result. Winding tension should be adjusted to allow for shrinkage if appropriate. Winding should extend 2 to 4 inches beyond perforations on beam with side-to-side movement to compensate for excessively large selvage buildup, if necessary.

Effect of moire

If moire develops, wind looser and run shorter O/I times. Pretreatment of lightweight polyester fabrics with caustic (6 to 8% owg) reportedly helps avoid moire. To correct moire on polyester, run at 240°F for 30 min., with carrier.

To avoid crocking problems with certain disperse reds on polyester (especially Disperse Red 53, 60, 132, 131, and 159), drop the bath hot. This will help to avoid crystallization o these disperse dyes when the bath cools. Dye paste-up procedures and bath stability are critical for beam dyeing just as for package dyeing.

Jet dyeing machines have many advantages over other equipment, including:

- better heat distribution;
- higher turnover rate which allows use of brine and faster rate of rise; and,
- does not have bath stability problems like package and beam machine.

Problems which can arise with jet dyeing include harsh action and fabric distortion of some machines, tangles which can result from foaming due to certain dyes or excessive use of chemical auxiliaries, bath breakouts from shearing or temperature effects, and shading port-to-port due to uneven strand length. One common error in jet-dyeing practice

Table IX: Beck Audit—Mechanical Inspection

Reel type, shape, cover, speed—compatible with substrate and dye recipe
Idler reel—turns free and true
'Snags' or rough edges in the machine
Tangle detector—rake and reel overload
Tangle alarm—audible and visible
Controller accuracy—temperature and rate of rise
Leaking valves—drain, fill, steam types
Steam quality available (while other demands are "on")
Circulating pump and heat exchanger (if any)—performance *at operating temperature*
Location and integrity of temperature sensor
Location and evenness of steam injection for heating
When heating and also when holding at 140° and 200°F, front-to-back and end-to-end temperature differences
Overhead steam (if any)
Damper and door (front and rear) operation
Verify damper ability to exhaust fumes
Fill water temperature

Table X: Beck Operations Checklist

Load out the entire length
Load size—60 to 80 pounds per beck foot (typical)
Long strands dye light, short strands dye dark, be sure all of the strands are the same length
Load out fully and evenly
Sew seams straight, no twist in strands, no holes in seam
Control the liquor level according to the fabric; too high gives tangles and "swimming" of cloth, too low gives abrasion, streaks, blotchy dyeing
Schedule light shades first, dark shades later
Base electrolyte and buffer on the bath, not the cloth
Ensure moderate ballooning by allowing some foam or air to collect inside tubular goods—inflate with airhose if needed
Be sure to take a slow rate of rise near the critical points, such as wet T_g and dye strike temperature
Don't boil a beck—tangles will result
Use overhead steam to prevent drips —especially in winter
Be sure doors and dampers are closed when running at high emperature to avoid cracks and drips
Be sure goods have adequate turnover rate—once per minute is typical.

[Continued from page 26]

is the excessive use of chemical specialty-dyeing assistants. Usually very few chemical specialties are needed.

Conclusion

It is beyond the scope of this or any other single article to specifically address all possible troubleshooting situations in batch dyeing. But this article is intended to provide some means of accomplishing problem solving in a wide variety of batch dyeing operations. ☐☐☐

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