Pollution Prevention Seminar

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Color Residues in Dye Wastewater

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It is widely recognized that color in textile dyeing and printing wastewater is a significant problem which must be addressed. (Houser 1994, Cooper 1989, Wagner 1994, Smith 1994 CHMR, Horning 1977) Although color is only an aesthetic pollutant, it is very easily visually detected, and even trace quantities of commercial textile colorants in wastewater are readily evident. Although there are many methods of color removal, none works across the board. (Koonce 1993 Masters Thesis NCSU) Therefore color is a great concern nowadays, with fiber reactive and sulfur dyes for cotton leading the list of offenders. (Houser 1994) Because of difficulties in treating color, colored chemical compounds must be eliminated by P2, since treatment is too difficult and expensive to meet future regulations. (Cooper 1989)

Measuring Color

Measuring color in textile wastewater is difficult at best.(Koonce 1993) If the wastewater sample is not filtered, then suspended solids interfere with transmission measurement, usually rendering it meaningless. If the sample is filtered, then the resulting measurement does not accurately reflect the perceived appearance of the wastewater, due to the removal of the appearance of turbidity. There are several measurements which can be made, including the following: Color, Apparent Color, and Turbidity.

"Color" (two methods - ADMI and APHA), a measurement of the color of transmitted light through a filtered wastewater sample, resulting in a computed value of a single number characterizing overall color. The two methods show essentially no correlation on textile wastewater. "Turbidity" is a measure of the light scattering from the liquid sample. Apparent color is a measurement which attempts to combine the two.

Due to extremely high variability of tinctorial characteristics of dyes solutions, it is not possible to generalize about how much dye (in % or ppm) would produce a specific color perception, or color value on the ADMI, APHA, or turbidity scale. Worse still, many regulations are written in terms of "no appreciable change in the color of the receiving waters", which really leaves a mill completely in the dark, so to speak, as to what is permissible in the waste stream itself.

The source of color residues

Dyes and pigments are highly colored materials used in small quantities (eg a few percent or less of the weight of the substrate) to impart color to textile materials for aesthetic or functional purposes. (AATCC 1981 Dyeing Primer page 4) In typical dyeing and printing processes, 50 to 100% of the color is fixed on the fiber, and the rest is discarded in the form of spent dyebaths of less than complete exhaustion or as wastewater from subsequent washing operations. (Wagner 1994) The term exhaustion refers to the amount of dye which disappears from the bath during a batch dyeing, and is sorbed in/on the fiber. The term fixation refers to the amount which is more or less permanently attached to the fiber in the sense that it must first exhaust, and then it must not wash off in the afterwashing part of the dyeing process.

Since the mid 1800's, dye chemists have sought to fulfill consumer demand for dyes with outstanding permanence, ie unaffected by crocking (rubbing), exposure to light, oxidizing or reducing agents, attack by chlorine or ozone, hydrolysis, or essentially any other environmental factor in use. (Smith 1994 CHMR) Their success has resulted in dyestuffs of outstanding end use permanence qualities and by the same token, just about complete resistance to treatment.

Dyes are applied by either continuous or batch (exhaustion) processes. In the former (continuous dyeing or printing), dye solution or print paste is continuously applied to a substrate (usually fabric), then is fixed on the fabric by chemical reaction, steam, heat or other mechanism. In the latter (batch or exhaust dyeing), a dye solution is brought into contact with a substrate. Due to the natural affinity of the dye for the substrate fiber, the dye migrates over time into the fiber, tending toward an equilibrium. After the exhaustion phase, some dyes require subsequent chemical baths for the purpose of fixing the dye on the substrate. In continuous processes, low affinity dyes are preferred since an attraction of the dye for the fabric is not necessary. In batch processes, high affinity dyes are necessary, since affinity is the means by which the dye exhausts into the substrate.

Dyebath Exhaustion - The Basics

Two basic actions will minimize color discharges. First, dye handling must be optimized to eliminate spillage, machine and implement clean up, discards, etc. Second, exhaustion from dyebaths and fixation must be maximized and wash off minimized. To maximize dye exhaust (E), two main factors are important: affinity (K = partition coefficient) and bath ratio (L). This analysis applies only to dyes which do not react, or to reactive types during the exhaustion phase prior to beginning of reaction. Typical values are

K	50 - 1,000 for various dye/fiber combinations
L	5 to 50 for various machines (Smith 1989 AWBook...)
E	0.50 to 1.00 (50% to 100% exhaustion) (Wagner 1994)

K is a partition coefficient, is the ratio of concentration of dye in solution to concentration of dye in substrate at equilibrium, ie

$$K = c^f / c^s$$

where

c^f = concentration of dye in fiber at equilibrium and
c^s = concentration of dye in solution at equilibrium.

An important relationship is

$$E = K / (K + L)$$

When L increases, E decreases and more color is discharged. This effect is more pronounced on low affinity dyes, ie when K is low. When affinity (K) decreases, the dye remains more in the solution and the color in the wastewater increases, especially if L is high.

Each dye class is applicable to different fibers, and dye classes vary in their affinity for those fibers. Also within dye classes, individual dyes show large variations. Thus, any typical exhaustion data must be taken in a very general way. With that caveat in mind, typical exhaustion/fixation Typical fixation levels for various dye types are given as follows. (Wagner 1994)

Class	Typ. K	Typ. Fixation	Fibers Typically Applied to
Acid	114	80 to 93%	Wool, Nylon
Azoic	210	90 to 95%	Cellulose
Basic	663	97 to 98%	Acrylic
Direct	80	70 to 95%	Cellulose
Disperse	104	80 to 92%	Synthetic
Premets	469	95 to 98%	Wool
Reactive	32	50 to 80%	Cellulose
Sulfur	32	60 to 70%	Cellulose
Vat	119	80 to 95%	Cellulose

Note: In the above, K is conmputed by assuming
a bath ratio of 17:1 (typical for becks).

As can be seen from the above, cellulose dyes are the greatest problem in terms of poor exhaustion and fixation characteristics, with the very popular fiber reactive types leading the list of poor fixation.

Factors beyond dyebath exhaustion

Work practices in the mix kitchen, cleaning operations, scheduling, disposal of obsloete inventory, etc are extremely important in a well organized P2 program.

Fixation and afterwashing are also very important steps in the overall scheme of dyeing, and are closely related to color in wastewater. There are many methods of fixing, including chemical insolublizing of the dye by oxidation or coupling (vat, sulfur, naphthol), chemical reaction of dye with the fiber to form covalent bond (fiber reactive), reaction of the dye with the fiber to form an ionic bond (acid, basic), formation of solid solution (disperse), and finally the use of fixative agents (direct, fiber reactive).

Washing is a very important step from a quality point of view, and deserves attention. The important points are the role of bath ratio in drop/fill wash procedures, and the control of flow and mixing in overflow washing. Also there are very effective special methods such as countercurrent washing.

Fiber Reactive Dyeing

Poor fixation has been a long standing problem with fiber reactive dyes. (Cook 1991) Batch dyeing of fiber reactive dyes clearly represent the greatest challenge in terms of minimizing color in the effluent. Considerable research and development emphasis in now being placed on this issue. For the typical mill dyer, it pays to understand the fundamental principles behind fiber reactive dye fixation efficiency.

Typical fiber reactive batch dyeing processes include "all in" and "two step" process. The general procedures are

Two step	All in
Fill machine	Fill machine
Set bath	Set bath
Load fabric	Load fabric
Add dye	Add dye
Start heating	Add salt
Add salt	Add alkali
Attain dyeing temperature	Start heating
Run 10 minutes	Attain dyeing temperature
Add alkali	
Run 30-45 minutes	Run 30-45 minutes
Hot patch decision	Hot patch decision
If OK, wash	If OK, wash
Cold patch decision	Cold patch decision
Drop bath and unload	Drop bath and unload

In the two step procedure, the dyeing is in a reversible exhaustion mode until alkali is added, at which time the dye starts reacting. Since the dye is relatively more exhausted at the onset of reaction, it is more likely to react with fiber. In the all-in process, there is no initial exhaustion, and the entire dyeing process is a non-reversible simultaneous diffusion and first order reaction. The all-in process, of course, results in lower percent fixation and thus more color in the wastewater.

The bireactive "double anchor" dyes now being promoted to reduce wastewater color, even when they are applied by the two step process, do not get the full expected fixation from the second reaction because almost all of the dye hydrolysis occurs in the solution, and thus the second reaction is always an all-in type of situation.

The key to getting high fixation (thus less color in wastewater) in batch dyeing of fiber reactives is to get high exhaustion by

using high affinity dyes
using low bath ratio dyeing machines
getting maximum exhaustion **before** adding alkali
allowing sufficient time for full fixation
using proper temperature, salt and alkali concentrations

For some dyes, notably the "vinyl sulfone" types which react by Michael addition mechanism, the activation energy for the hydrolysis reaction is not as great as the activation energy for the reaction with cellulose. Thus (based on the Arrhenius equation), raising the temperature on these will cause the hydrolysis reaction to increase in rate faster than the reaction with cellulose, leading to more hydrolysis. The triazines, on the other hand, react by a nucleophilic <u>substitution</u> reaction (not addition) and thus have the same activation energy for water and for cellulose. So the temperature is not as critical (in terms of color discharges).

<u>Factors affecting fixation of FR dyes</u>
This is an extremely complex subject and widely misunderstood. Theoretical models can be set up, but they are all based on very primitive assumptions (eg plane slab of substrate, etc) to simplify the differential equations and boundary conditions. Also, even in those simplified cases, the resulting differential equations can not be solved exactly.

Wagner 1994 and Cook 1991 correctly assert that Cibacron "C" bireactive dyes (dyes which have the ability to react twice, ie "double anchors") have higher fixation, but they fail to point out that the reason for this is not their bireactivity per se, but rather the fact that the recommended application procedure calls for up to 120 g/L of salt to boost exhaustion. The reasoning is that reasoning is that 75% of the dye will be fixed by the first reaction. Then, of the 25% that did not fix to the fiber in the first reaction, 75% of that will fix to the fiber in the second reaction. But one must also take into consideration that the 75% which reacts with the fiber in the first place did so because it is in the fiber, and the 25% that did not react with the fiber in the first reaction did not do so because it is in the solution. When the second reaction occurs for that 25%, what will it react with? It will react with whatever it is in. Therefore the second reaction of the 25% will be more likely to be with the solution (a second hydrolysis), since that's where it is. This dye will not be fixed. Thus, the real reason that the bireactive dyes have higher fixation is that the recommended salt levels are about 50% to 100% higher than normal (up to 120 g/L). The bireactivity helps some, but is not the main factor.

The problem of estimating fixation is one of simultaneous diffusion and first order kinetics reaction. In spite of the inability to solve these equations exactly, the equations themselves and several experimentally verified data show that there are three main factors that are important. (Fiber shape is also important, but not controllable by the dyer.)

The three main factors that influence fixation efficiency of fiber reactive dyes are

Process design (two-step vs all-in)
Dye affinity / low bath ratio / maximum exhaustion
Dye reactivity

Although there are many different kinds of fiber reactive dyes, in each case, there are two competing reactions

Dye + water => hydrolyzed dye (washes away as color in wastewater)

Dye + fiber => desired colored textile material

The fixation efficiency is the ratio of the dye fixed (desired reaction) to the dye hydrolyzed (undesired reaction). (Preston 1986). A fairly straightforward kinetic analysis leads to the equation

$$E = \frac{S}{L} \frac{[\mathrm{D}]_{\mathrm{F}}}{[\mathrm{D}]_{\mathrm{S}}} \sqrt{\frac{D}{k'_{\mathrm{H}}} \frac{R_{\mathrm{F}}[\mathrm{CellO}^-]}{[\mathrm{OH}^-]}}$$

where

E = fixation efficiency
S = fiber shape factor (fixed)
L = bath ratio
$[D_f]/[D_s]$ = instantaneous partition, a factor similar to K above
D = diffusion coefficient, related to K
k'_H = dye reaction rate constant
R_f = ratio of reaction rates (cellulose/water), usually about 1
$[\mathrm{CellO}^-]$ / $[\mathrm{OH}^-]$ = ratio of ionization constants of cellulose to water, a number about 30 (cellulose ionizes about 30 times more completely than water)

In a typical dyeing, S, L, R_f are constant. K and k are known or can be determined for each dye and D can be estimated from a graph of log K vs log D (see Peterson 1986 page 155 figure 4.8) to be a constant times $K^{-1.25}$. Based on this, and lumping all the constant (fixed) terms into one, you can get a relationship that is approximately

$$\text{Efficiency of fixation} = (\text{ A constant }) * (K^{1/3}) / (k^{1/2})$$

Using Conventional Fixatives

Standard practice in direct dyeing is to use conventional dye fixatives to improve the resistance of direct dyes to washing off in the afterwashing steps as well as in various fastness tests. The use of fixatives is however not as prevalent on fiber reactive shades, except in yarn dyeing. Fixatives are effective on fiber reactive dyes, and can cause the fixation of hydrolyzed color which otherwise would wash off, thus reducing color in wastewater.

Screening of Dyes
In view of the variability of dyes within a given class, many dye companies have reassessed and reevaluated the performance of their dyes with respect to the environmental performance, especially metal content, salt requirements and color discharges. Alternatives exist, including bifunctional reactive dyes. (Houser 1994) These dyes give enhanced fixation due to their bireactive nature, but at the expense of a higher recommended salt loading. Presumably in the future, dyes with enhanced affinity will be developed, which will provide even better fixation properties.

Auxiliaries
Most specialty chemicals / dyebath auxiliaries contain surfactants which increase the solubility of dyes in water, thus retard their exhaustion. There are over 5000 such products in use. (Smith 1987 Chemical Screening and Inventory Control) These should be used very sparingly, since they produce not only color but also BOD and other pollutants. In most cases, it is possible to properly dye a substrate with little or no dyebath auxiliaries if the time, temperature, salt, pH and mechanical factors are properly set.

Pad Batch and Dyebath Reuse
No discussion of reducing color discharges in textile waste water would be complete without discussing the pad batch method and dyebath reuse. A write up on pad-batch is attached.

P2 Strategies - Summary
With the foregoing background, there are many actions which can be taken by a mill to reduce color in the wastewater. In every case, process optimization to get the highest possible fixation is the key. (Wagner 1994) The strategies vary between batch and continuous, because getting better fixation in batch dyeing is related to a combination of exhaustion and fixation, but for continuous, only fixation is important.

Batch
In terms of batch dyeing, the main area for concern is cellulosic dyeing. In the general design of cellulosic batch dyeing processes, the most important factors are:

Good cloth preparation (Peterson 1986)
Use Low bath ratio
Select high affinity dyes
Optimize pH and salt, if used, for each recipe
Use proper time-temperature profile relationship
Avoid auxiliaries that retard exhaustion
Minimize use of auxiliaries, surfactants
    Avoid adding more chemicals (eg defoamers) to offset undesired side effects of others. Alternatives include procedural or mechanical remedies, or changing the dye selection or the product itself.

Dyebath Reuse and Pad-Batch Dyeing

VII.5.2 Dyebath Reuse

Dyebath reuse is not a new idea. Prior to the 20th century, no dyer worth his salt would have discarded a dyebath--dye was too hard to come by to casually discard to the river. During the War Between the States, the Confederate government used dye brought in on blockade runners as payment for textile goods for military uniforms. There was little other source of dyes. But the availability in the 20th century of easy to obtain (and cheap) synthetic dyes as well as certain marketing demands (exceptional shade repeat consistency) dictated changes in procedures in attitudes, leading to the

The idea of dyebath renovation and reuse began attracting attention around the middle 1970s

Table VII.5.1.c-1: Dyeing Machinery Liquor Ratios and Water Consumption

Dyeing machine	Typical liquor to goods ratio	Water consumption gallons per pound
Continuous	1:1	20
Beck	17:1	28
Jet	12:1	24
Jig	5:1	12
Beam	10:1	20
Package	10:1	22
Paddle	40:1	35
Stock	12:1	20
Skein	17:1	30

VII.5.1.d Wastewater Recycle in Preparation

Preparation processes, especially desizing and scouring, can be done on many types of equipment, both continuous and batch. These are usually the largest water consumers in a mill. The continuous processes have great potential for wastewater recycle/reuse since the waste stream is continuous, fairly constant in characteristics, and usually easy to segregate from other waste streams.

Examples of waste stream reuse in a typical bleach unit processing polyester/cotton and 100% cotton fabrics would include:

> recycle the J-box and kier drains wastewater to saturator
> countercurrent washing
> recycle wastewater from continuous scour operation for batch scouring

Of course, preparation chemicals (including especially optical brighteners and tints) must be selected in such a way that reuse does not create quality problems such as spotting.

The situation with batch scouring and bleaching does not allow, in general, for recycle/recovery of waste streams because:

> streams occur intermittently
> streams generally dump into pits and are not easily segregated
> liquor ratios are much higher in batch preparation; therefore, the wastes are more dilute
> preparation steps are frequently combined

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when energy costs became a critical factor in overall manufacturing costs. Dyebath renovation and reuse has been shown to be a feasible method of cost reduction, energy savings, and waste source reduction in some textile wet processing applications. Laboratory studies, pilot plant work, and full scale commercial use have been documented. This section summarizes these documented studies and presents typical examples of comparative procedures; however, this technique has not really caught on in commercial production.

As early as 1964, it was estimated that about 10% to 16% of textile wet processing wastewaters were reclaimed or recycled. Modern water and energy conservation practices, including strategies such as dyebath reuse, make it possible for wet processors to increase this figure dramatically, with corresponding cost savings and waste reduction.

Dyebath reuse is an attractive alternative to pretreatment systems for dyehouses that discharge to POTWs. In many cases, dyehouses operating in cities do not have enough space to construct large pretreatment systems. Dyebath reuse, which has been shown to reduce flow, BOD, and COD loadings up to 33%, requires a smaller investment in equipment than pretreatment systems. Also, the dyebath reuse concept has a return on investment in the form of dye, chemical, and energy savings which pretreatment does not.

Savings, as well as installation costs and operating expenses, are site-specific. Based on case histories available to date, the data in Table VII.5.2-I generally summarizes the magnitude of these factors. The payback period is generally 13 to 20 months.

Table VII.5.2-I:
Typical Cost and Savings Figures
for Dyebath Reuse (per Dye Machine)

Lab and support equipment (one set)	$ 9,000
Machine modifications/tanks/pumps/pipes	$20,000
Annual operating costs	$ 1,500
Annual savings (total)	$21,000
Dyes and chemicals	$15,000
Water	$ 750
Sewer	$ 750
Energy	$ 4,500

VII.5.2.a Dyebath Reuse Procedure

As can be seen from the following procedures, the changes required for dyebath reuse are straightforward. Dyebath reuse consists of 4 steps: store, analyze, reconstitute and reuse.

1. Store the spent dyebath in a tank or move to a second identical dyeing machine. One interesting application of dyebath reuse involves moving the dyebath back and forth between two or more machines. For example, package dyeing machine (A) can be preparing yarn while a second identical machine (B) is in dye. When B completes its dye cycle, the bath is pumped to A for renovation and dyeing. In the meantime, the yarn in B is after scoured, unloaded, and a new batch is loaded and prescoured. By that time, A has finished dyeing, and the bath goes back to B for another reuse cycle, etc.

2. Analyze or estimate the dye and chemical content of spent dye liquor using a spectrophotometer and/or guidelines based on specific production experience. Equipment for this is commonly available at a cost of under $10,000. Unexhausted dyestuff is measured by solution coloristic measurements, sometimes using extraction techniques if the bath is turbid. Chemical losses are determined by specific production experience based on exhaust, volatilization, and dye liquor carry-off with the dyed substrate (usually about 10 to 15%). Chemical losses may be estimated or determined analytically if appropriate equipment is available. Usually the quantities are not as critical as the dye, and an estimate is sufficient. The procedure for extracting dye from the dyebath is as follows:

   Add 20 ml (25 grams) of salt, 25 ml of exhausted dyebath, and 25 ml of a solvent such as 1-octanol or toluene in succession into a clean separatory funnel. Place stopper in funnel and shake vigorously for 30 seconds. Allow contents to separate for 30 seconds. Shake vigorously again for 30 seconds. (This mixing action results in extraction of dyes from the dyebath water into the solvent.) Place funnel on ring stand and allow for distinct separation of salt (bottom layer), water (middle layer), and solvent with dyes (top layer). Solvent layer may appear cloudy due to water in the solvent. Remove stopper. Open the stopcock and allow the salt and water layers to drain out to sink. Close stopcock. Place two cotton balls in clean, dry syringe. Drain solvent layer from funnel into syringe. Allow solvent to pass through cotton balls in syringe to absorb any remaining water, and collect sample in a clean, dry sample cell as it leaves the syringe.

3. Reconstitute by adding make-up amounts of dyes and chemicals to renovate the spent bath. Also add water to make up the volume that is carried off by the dyed substrate.

4. Reuse the bath for another dyeing. Because the used dyebath will usually be hot (over 140 F), it must be cooled down to an appropriate temperature for starting the next dyeing. Considerable time and energy are saved by starting the next dyeing at the highest possible temperature consistent with desired quality factors. This is one of the main advantages of dyebath reuse. The ultimate "life" of a dyebath varies according to the quality required, contaminant buildup, and other factors.

VII.5.2.b Dye Classes and Potential for Bath Reuse

There are many different classes of textile dyes, and each class applies to specific fiber types and requires different exhaustion procedures, specialty chemicals, pH, equipment, *etc*. Because of these differences, savings vary. Also, results may vary with respect to the fastness, shade reproducability, and other factors. Batch dye systems have been reported to be adaptable to dyebath reuse as shown in Table VII.5.2.b-I.

As of this date (July 8, 1992), no case history has been published for direct dyes on cellulose; however, this could also be done and would result in chemical savings of salt, leveler/retardant, dye, surfactant, lubricant, and defoamer. Dyebath reuse is limited by contaminant buildup of two types: (1) fabric impurities not removed during preparation, and (2) emulsifier systems, wetters and dispersants eg from dye, retarder. If these can be monitored and controlled, dye reuse is possible for 15 or more cycles.

A laboratory study of reuse of disperse dyes on 100% polyester spun yarn (package dye) showed that nine reuse cycles could be expected, with savings of about 80% on water and chemicals, and about 40% on energy.

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Table VII.5.2.b-I: Systems for Dyebath Reuse

Product	Fiber	Dye class(es)	Machine
Knit fabric	Polyester	Disperse	Jet
Knit fabric	Cotton	Reactive or direct	Beck
Knit fabric	Poly/cotton	Disperse/reactive	Beck
Knit fabric	Poly/cotton	Disperse/direct	Beck
Yarn package	Polyester	Disperse	Package
Yarn package	Poly/cotton	Disperse/reactive	Package
Yarn package	Poly/cotton	Disperse/direct	Package
Socks	Nylon/spandex	Acid	Paddle
Pantyhose	Nylon/spandex	Disperse/acid	Beck
Carpet	Nylon	Disperse/acid	Beck
Carpet	Polyester	Disperse	Beck
Woven fabric	Aramid	Basic	Jet
Skein	Acrylic	Basic	Skein

VII.5.2.c Limitations of Dyebath Reuse

To gain the maximum benefit from dyebath reuse, users must keep certain considerations in mind. The easiest systems to manage for dyebath reuse are dye classes that undergo minimum changes during the dyeing processes eg acid dyes for nylon and wool, basic dyes for acrylic and certain copolymers, direct dyes for cotton, and disperse dyes for synthetic polymers.

A higher degree of difficulty can be expected from other classes (vat, sulfur, fiber reactive). The easiest situation to manage is the reuse of a dyebath to repeat the same shade with the same dyes and equipment on the same fiber. It is also possible to reuse a dyebath to produce a darker or lighter shade with the same dyestuff selection on the same fiber. More difficult situations would involve addition of new colorants to renovate a dyebath. This would lead to potential problems with shade matching and metamerism.

The number of reuse cycles for a dyebath is limited by buildup of impurities. These impurities can come from several sources. One source is fabric impurities from incomplete preparation, which include natural impurities in cotton and wool, knitting oils, winding waxes and emulsions, fiber finishes, size materials and the like. Impurities can also accumulate from dye diluents, salt buildup from addition of acids and bases for pH control, steam contaminants for direct steam heated baths, and emulsifier systems from exhausted chemical specialties. Many impurities are surfactants, and these can cause stripping and/or retarding of dye exhaust if allowed to buildup excessively. Other problems such as spotting and excessive foaming can occur if too many reuse cycles are attempted. The usual range of reuse cycles if 5 to 25, and each process and/or shade must be optimized by actual production experience.

Specialty dye assistants and other materials which are essential to a dyeing process may be lost by several mechanisms. These include losses due to vaporization from open dyeing machines, exhaust onto the fabric, chemical reaction, and drag-out by the substrate. These losses may vary from 10% upward and may vary between components of a blended chemical specialty. To insure best results, dyeing assistants must be carefully screened for reuse performance.

One major reason for using batch (exhaust) dyeing is the ability to produce small lots, short runs, and fast turnaround times. Because dyebath reuse requires special scheduling considerations, it may somewhat limit the flexibility of batch dyeing operations.

In summary, batch dyebath reuse may not be for every situation; however, the economic savings are large, if properly applied, and the waste reduction is substantial when this technique can be used.

VII.5.2.d Case History #1

Perhaps the most extensive and best documented study on dyebath reuse was carpet dyeing done by Bigelow in the summer of 1983. In this work, carpets were dyed with conventional (Procedure VII.5.2.d-A) and with dyebath reuse (Procedure VII.2.6.d-B). Results of quality, savings, and waste reduction were carefully documented in detail. Some of the more interesting data relating to waste reduction show that BOD and COD were reduced by over 30%, and phosphorous, phenolics, and total dissolved solids were reduced by 50% and 80%. Dyeing in Bigelow production runs were done on two different shades and styles of carpet. A pair of conventional atmospheric becks were used, and dyebath was pumped back and forth between them. Over twenty reuse cycles were obtained in this case. Savings were estimated to be over $60,000 per year per pair of becks.

VII.5.2.d.1 Procedures for Carpet (Dyebath Reuse)

Conventional Carpet Dye Procedure

1 With drain closed, load carpet into beck using spray to assist in moving carpet over reel
2 Fill beck with cold water
3 Add auxiliary chemicals; continue mixing for five minutes after all chemicals are added
4 Measure pH and adjust if necessary
5 Add dyes and mix for 10 minutes
6 Raise dyebath temperature to 180 F at 3 F per minute
7 Dye at 180 F for 30 minutes
8 Patch; if necessary, perform add(s) After each add, run 15 additional minutes
9 Add cold water with drain open to cool to 150 F or lower, shut off water and drain beck
10 Close drain and fill beck, cold water to rinse, cool, and float carpet
11 Drain and flush beck to prepare it for next dyeing

Modified Procedure for Dyebath Reuse

1 With beck drain open, load two rolls of carpet onto beck using spray rinse (tint added to greige carpet is removed from carpet yarns during spray rinse; for reconstituted dyeings, the drain is left open to prevent tint buildup in recycled dyebaths)
2 Close drain; Arrange and connect dyebath transfer equipment into appropriate orientation; Set flowmeter totalizer to zero; Pump dyebath to new beck from beck used for previous dyeing
3 Add auxiliary chemicals to beck; continue mixing for five minutes after all chemicals have been used
4 Measure pH and adjust if necessary
5 Add dyes and mix for ten minutes
6 Raise dyebath temperature to 180 F at 3 F per minute
7 Dye at 180 F for 30 minutes
8 Sample and, if necessary to obtain acceptable dyeing, perform add(s) (After each add, run 15 additional minutes)
9 Add cold water with beck drain closed and cool to approximately 140 F. (Some exhausted dyebath will be lost through overflow ports.) Collect dyebath sample for absorbance measurement. Pump to new beck (Step 2 of subsequent dyeing cycle). Perform solvent extraction of dyebath sample, perform absorbance measurements and calculate amounts of

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dyes and auxiliary chemicals required for next dyeing. Drain.
10 Close drain and fill beck, cold water to rinse, cool, and float carpet
11 Unload carpet, then drain and flush beck to prepare for next dyeing

VII.5.2.d.2 Pollution Reduction Results - Dyebath Reuse for Carpet

The documented pollution reduction in this case is shown in Table VII.5.2.d.2-I below.

Table VII.5.2.d.2-I: Pollutant loading

Pollutant	Conventional	Dyebath Reuse	Reduction
BOD (g/kg)	23	15	35%
COD (g/kg)	56	39	30%
TSS (g/kg)	0.53	0.26	51%
TDS (g/kg)	31	14	55%
Phenolics (mg/kg)	1.5	0.8	47%
Total-P (g/kg)	2.8	1.0	64%

VII.5.2.e Case History #2

Adams-Millis Company implemented a practical dyebath reuse procedure in plants at High Point and Franklinton NC. In both cases, nylon pantyhose were dyed in rotary paddle machines with disperse dyes. The results were so good that 95% of the rotary drum machines at the Franklinton plant are reportedly run dyebath reuse systems.

The idea of reuse was also used in these operations in another way. The final softener bath was reused as a prescour for the next batch to remove oils, fiber finish, etc., before dyeing. Cost savings were estimated at $0.02/pound of goods produced.

VII.5.2.f Case History #3

Evans & Black Carpets instituted dyebath reuse at its Dalton GA, plant for the disperse dyeing of nylon carpets. The result was a projected savings of $115,000 annually to the mill using eleven becks. At the time the study was published, 45% of the plant's production was reportedly dyed with reused baths. It was confirmed in this production situation that buildup of surfactants during the repeated reuse cycles causes slight decreases in the disperse dye exhaust. In general, this can be compensated by increasing the dye concentrations slightly as reuse cycles increase.

VII.5.2.g Case History #4

Basic dyes are normally exhausted from acidic baths for acrylic and certain other copolymer materials. One case history relating to dyeing basic dyes on Nomex in jet dyeing machines is available. Full procedures and results have ben published.

In these plant trials, dyebaths were reused up to 15 times successfully. Capital expenses to install the equipment necessary to accomplish dyebath reuse were determined to be about $15,000. Savings were estimated to be $120 to $140 per dye cycle (500-700 pounds) for a cost reduction of $0.17 to $0.28 per pound. The annual savings to the mill was estimated at $100,000.

In this data, like the Adams-Millis study, there was uneven depletion of various components of dye carrier during the dye process. This required a reconstitution of 65% for dye carrier compared to

10% for other chemicals.

VII.5.2.h Case History #5

Acid dyeing of nylon carpet using reconstituted dyebaths was done on atmospheric becks. Dyebath reuse was limited to 10 cycles due to buildup of salt. This reuse led to an annual savings estimated at $31,300 compared to a total cost of $15,000 for installation of necessary equipment.

VII.5.3 Pad/Batch Dyeing

Two of the major problem areas facing the cotton segment of the textile manufacturing industry in the next few years will be the elimination of color and salt from dye wastewater. At present, application of the very popular fiber reactive dyes for cotton require massive amounts of salt, approximately equal to the weight of goods processed. An attractive alternative for application of fiber reactive dyes is pad/batch dyeing. By using this application method, pollution concerns can be addressed without giving up the outstanding properties of fiber reactive dyes, and with considerable improvement in productivity and energy savings.

The pad/batch (cold) method of dyeing cellulosics is hardly a new concept. It has been quite successful in a wide variety of applications. In many ways, it is one of the most reliable and easiest to control methods available today for certain applications. Strangely enough, however, it has not caught on in this country to the extent that it is used in other parts of the world.

To quickly summarize the pad batch method, prepared fabric is impregnated with liquor containing premixed fiber reactive dyestuff and alkali; excess liquid is squeezed out on the mangle; the fabric is batched onto rolls or in boxes, and covered with plastic film to prevent absorption of CO_2 from air or evaporation of water, then stored for two to twelve hours. The goods can be washed off in any of several conventional ways, depending on equipment available in the mill. The method is interesting because it offers several significant advantages, primarily in its waste reduction, simplicity, and speed. Production of between 75 and 150 yards per minute, depending on the construction and weight of the goods involved, is common. In fact, this kind of speed can make the limiting factor the wash-off facilities, which may not be able to keep up. Another factor that has generated enthusiasm for pad batch is its flexibility, compared to a continuous range. Either wovens or knits can be done, and in many constructions. Frequent changes of shade are no problem because reactives remain water soluble, making cleanup easy. This fits many situations well, especially when versatility is required.

Production case histories have shown that pad/batch dyeing for cotton, rayon and blends conserves energy, water, dyes and chemicals, labor and floor space. Salt consumption is reduced from about 100% on weight of goods to zero. Water consumption for pa d batch dyeing with beam wash-off is typically under two gallons per pound of dyed fabric, compared to typically 20 or more gallons on atmospheric becks for the same fiber reactive dyed shades. Energy consumption is similarly reduced from about 9000 BTUs per pound of dyed fabric for becks to under 2000 BTUs per pound for pad batch with beam washing. Chemical use, including alkali as well as specialty chemicals with associated BOD and COD loadings for waste streams, can be reduced up to 80% compared to atmospheric becks. Labor costs are also reduced. For example, two workers per shift can dye 200,000 pounds of fabric per five day week.

VII.5.3.a Dyes for Pad/Batch Dyeing

In general, the quality of pad batch dyeings is equal to or better than other dyeing systems. Specific cost information is shown in Tables VII.5.3(a)-1, -2 and -3. These were prepared and

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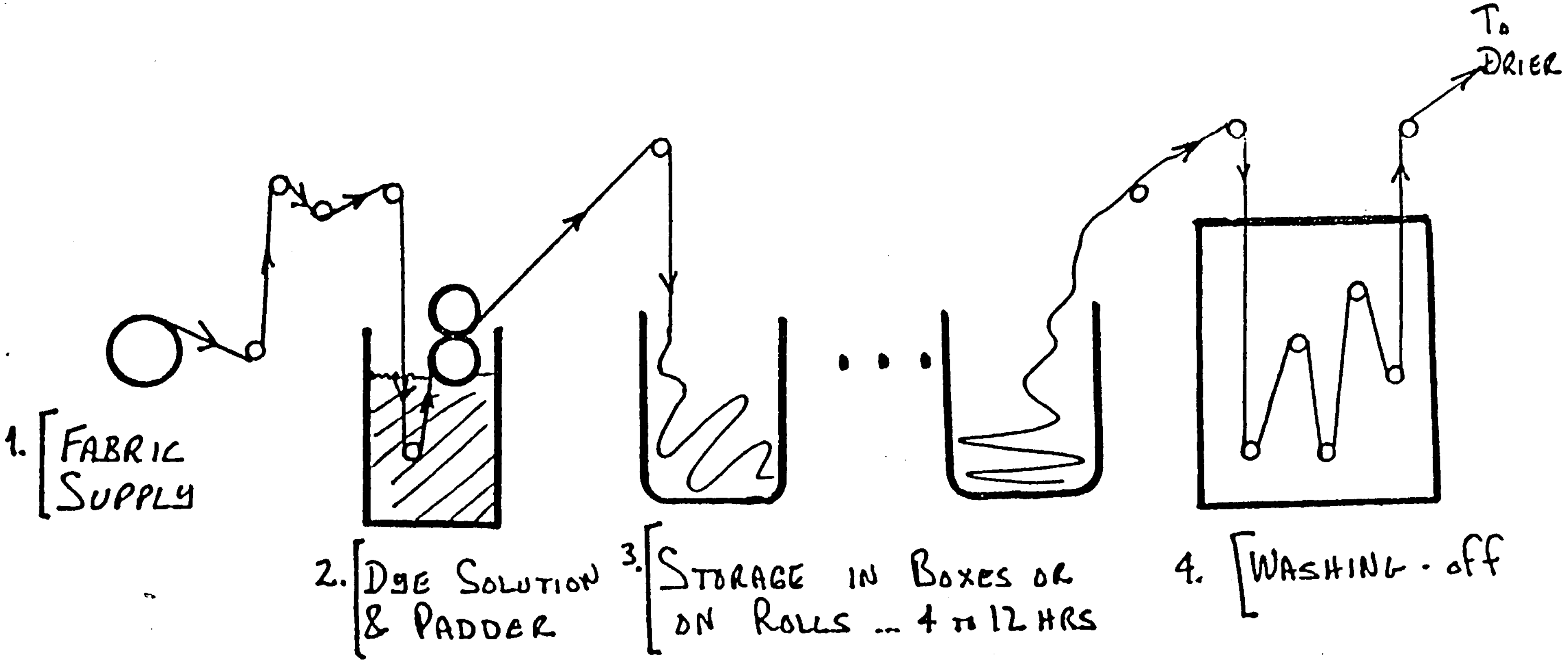

Pad/Batch, Storage and Wash-off Unit

originally published by Cotton Incorporated. Pad batch dyeings require highly reactive "cold dyeing" fiber reactive colors. Examples of brand names of such colors are:

Atlafix CX (Atlantic)
Cibacron F (Ciba Geigy)
Drimarine K (Sandoz)
Levafix E (Mobay)
Intracron C (C & K)

Procion MX (ICI)
Remazol (Hoechst)
Sumafix (Wright)
Levafix E...-A (Mobay)
plus any other "cold dyeing" type

VII.5.3.b Equipment for Pad/Batch Dyeing

Equipment for pad/batch dyeing consists of:

> mix tanks, drug room equipment
> padding unit
> batcher or material handling system
> dye/alkali mixing device
> A-frames, storage racks or storage boxes
> wash-off device (beam, beck, continuous)

Pad/batch dyeing gives much lower defect levels than rope dyeing on many styles. For example, if dyed by exhaust methods on becks using direct dyes, fabrics of varying thickness, such as 100% rayon jacquard tablecloths, are difficult to process in rope form without streaking. Lower defect levels mean less redyeing, less use of stripping agents, etc.

VII.5.3.c Cost Comparison - Pad/Batch vs Conventional

Considerable cost savings result from the use of less labor, less energy, less chemicals, less floor space as well as better quality (less reworks and seconds). A cost comparison is shown in Table VII.5.3.c-I.

Table VII.5.3.c-I: Comparison of Annual Operating Costs

		Pad/Batch 2 Machines	Conventional 19 Becks
Production	(lbs/week)	193,050	193,050
	(lbs/annum)	9,652,500	9,652,500
Labor costs		$ 79,560	$ 256,360
Fuel costs		$ 52,000	$ 272,000
Extra drying step		$ 48,300	$ 0
Water costs		$ 8,700	$ 98,500
Dye costs		Varies, see Table VII.5.3.c-III	
Chemical costs			
Salt		$ 0	$ 19,112
Alkali		$ 0	$ 82,820
TOTAL Operating Cost		$ 207,672	$1,047,520

Table VII.5.3.c-II: Comparison of Capital Investment Costs

Pad batch dyeing system:	Comprising pad entry, padder, mix tanks, dye/alkali pump, 2 beam wash-off stands, 10 wash off beams, rotation stand, cradle let-off scray.

Dye pad for knits with associated equipment	$ 160,000
Installation estimated to be 30%	$ 48,000
TOTAL Pad/Batch	$ 208,000

Traditional exhaust dyeing: 19 atmospheric becks of 1000 pounds capacity each.

Becks 1000 pounds capacity @ $30,000 each	$ 570,000
Installation estimated to be 30%	$ 171,000
TOTAL - Traditional Becks	$ 741,000

Table VII.5.3.c-III: Comparison of Dyestuff Costs [cents/pound]
Typical Dye Cost for Pad-Batch vs Same Dyes on Becks

Color	Pad/batch	Beck dyed	Color	Pad/batch	Beck dyed
Powder blue	30	40	Bright blue	55	70
Dark red	50	63	Light blue	37	58
Bright yellow	35	50	Dark green	46	70
Bright red	48	75	Navy	30	53

All the above costs are for dyeing only (for 100% cotton), not including preparation. All of the beck dyed costs are cold reactive. In the cases of blends, or if the beck dyes were direct, pad/batch would probably cost more and beck dyeing will probably cost less.

The beauty of the pad batch system using the high reactivity dyes is that a great deal of the dye fixes in 30 minutes, and the difference in depth between one hour and eight hours is negligible in many shades. This is one reason for the unusual degree of shade reliability and is important because the fabric near the core of the take-up roll is obviously first on and last off, and has actually batched longer than the outer layers.

Because of the low physical affinity of these cold dyeing reactives, they work extremely well for all continuous operations that include a padding sequence. Color yield (exhaustion and fixation) tends to be lower when dyeing in a long liquor, compared to high affinity dyestuffs such as vats. A worthwhile increase in fixation can be accomplished in a shorter liquor, as the Table below illustrates using a typical dye of the low substantivity group - in this case, CI Reactive Yellow 22.

Liquor-to-goods ratio	L=	30	20	10	5	2	1	0.6
% Dye fully fixed	%=	20%	27%	40%	53%	68%	73%	75%
Increased color yield*		265%	170%	82%	38%	7%	--	--

(* comparing pad batch at 100% wet pickup to dyeing at the tabulated liquor ratio)

Higher fixation contributes significantly to reduction of color in wastewater. There are other advantages of this rapid fixation and stability of shade which are obvious when compared to other methods. In jet, jig and beck dyeing, for example, the normal routine is to continue dyeing, shading if necessary, until the correct color is obtained. Dyehouse operators are seen constantly cutting swatches off the goods for inspection. Even when the dyer is satisfied with the color, it may be that all fixable color has not reacted with the cloth, so that each batch must be treated individually. Highly colored wastewater and shade variations are inevitable. With pad batch, however, experience has shown that if padding and batching temperatures are properly controlled, reproducability of shade is outstanding, and color in wastewater is reduced.

There is still another benefit of this rapid fixation. It is a minor point perhaps, and easily overlooked, but there is almost 100% reproducibility from lab to production shades. This means less time loss, less dumped color, and fewer remakes. The pad batch system may be home design, but it must feature accurate mixing and metering. Two tanks hold dyestuff and alkali solutions which are fed to a mix and dispensing mechanism with a proportioning device. The mix is then fed via a pump to the pad unit. By employing a hollow displacer, it is possible to keep the passage through which the fabric passes less than one inch wide. This keeps the volume of liquor very low, about eight gallons or less, and insures the rapid turnover of liquor so that dye decomposition is kept to a minimum. This is, of course, important because adding the alkali to increase reactivity also affects the stability of the liquor.In working with plant production pad batch units, the following four point checklist has been helpful in avoiding problems:

1 Keep good alkali control by insuring adequate mixing and/or metering techniques.

2 Adjust exhaust dye recipes for pad batch by keeping accurate data on liquor ratios. Keep the immersion long, the liquor ratio short, and the volume low in the pad.

3 Have good preparation. Actually, pad batch reliability has reached the point where it can be used as a check on the preparation. If something doesn't look right, most often it can be traced to mistakes in preparation.

4 Keep good temperature control, and especially avoid dyeing hot fabric fresh from preparation. Feed cold fabric to the pad or else the temperature will rise. During very hot weather, keep the mix cool with a cooling water jacket, or use ice in the mix. In very cold weather, batch cloth in insulated boxes.

Since many mills that have agreements with municipal sewage systems pay on some formula based on the content of BOD, COD or other undesirable contents of the effluent, the pad batch method employing cold reactives is also attractive from the waste source management standpoint. Reactives do not require reducing or oxidizing agents, as do vats or sulfurs. Reactive dyes require using massive amounts of salt when employed in becks, but in the pad batch method, cold reactives require no salt at all. The use of chemical specialties, such as lubricants, leveling agents, antimigrants, fixatives, defoamers and other specialties, by pad batch dyeing is usually not required. Small amounts of detergent are used in washing-off. In summary, excellent results have been obtained with the pad batch (cold) system utilizing high reactivity dyes. Dyers have experienced many benefits:

> high color yield
> low capital outlay
> low energy requirements
> high production speed
> reduced labor requirement
> reduction in waste loads in effluent
> outstanding reproducibility
> excellent penetration/leveling characteristics
> rapid fixation
> cost savings

At their inception in 1956, fiber reactives were noted for their exceptionally bright shades. However, the range has increased dramatically. The shade range now includes new dyes of muted tones aimed at shades that previously were considered the domain of direct, sulfur and vat dyes. Reactives have given a good account of themselves in terms of fastness and economy against traditional classes of dyes, and future prospects appear very bright indeed.