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## **Chapter 2**

### **Waste Categorization/Prioritization for the Textile Industry**

This chapter describes a general categorization scheme for wastes generated in the textile industry (Section 2.1) and numerous specific wastes or pollution issues that are considered priorities for the industry (Section 2.2). Section 2.1, "General Waste Categorization," provides a framework for thinking about different types of waste generated in textile operations and the general approaches applicable to each type. Section 2.2, "Specific Wastes or Waste Problems," addresses many specific waste types or waste problems for textile operations. These wastes may be produced in one or more textile process areas and thus may be cross-referenced to one or more sections in Chapter 4, "Pollution Prevention in Specific Textile Processes."

#### **2.1 General Waste Categorization**

This section describes four general categories of textile waste that are particularly suitable for reduction through pollution prevention measures such as material substitution, process modification, inventory control, better management techniques, recovery, reuse, and recycling. Each type of waste has specific characteristics that require different pollution prevention approaches. The four categories of wastes are:

- Dispersible wastes
- Hard-to-treat wastes
- High-volume wastes
- Hazardous and toxic wastes

##### **2.7.7 Dispersible Wastes**

Many wastes that are well contained when generated become highly dispersed once they are released or mixed with other wastes. It is important to segregate and capture such highly dispersible wastes at the source because removing them from a mixed waste stream requires substantially more treatment at greater cost and effort. Examples of these wastes in the textile industry include:

- Waste streams from continuous operations (e.g., finishing, dyeing, printing, preparation).

- Print paste (especially from screen, squeegee, and drum cleaning).
- Lint.
- Waste from coating operations (especially foam).
- Waste solvents from machine cleaning.
- Still bottoms from solvent recovery (especially dry-cleaning operations).
- Batch dumps of unused processing (especially finishing) mixes.

In each of these cases, facilities are generally able to capture the waste in its concentrated form for more efficient, cost-effective treatment. These wastes are often allowed to mix with other wastes, however, complicating collection, disposal, salvage, or recycle/reuse. Even if the waste does not have reuse or recycle potential, it can usually be collected and prepared for disposal much more easily if it is not diluted or contaminated.

Sources of dispersible wastes are widespread in textile wet processing:

- Pastes: Pastes generally come from printing and include oil/water pastes and acrylic polymers. Both types tend to gel and form lumps in drains. These wastes can be difficult to sample with automated equipment because of their tendency to stop up sampler lines, pumps, and filters.
- Lint: Lint can originate from many textile operations, particularly preparation, dyeing, and washing operations. Usually, removing lint is fairly easy using primary control measures such as filters, which can be placed in the circulation lines of dyeing machines and other equipment. The filters must be maintained and cleaned out on a regular basis to ensure proper operation. The collected lint usually can be dried and then landfilled or incinerated. Higher quality lint can be marketed.
- Solvent: Proper handling of solvents can make disposal much easier; once mixed with water, however, solvents become difficult to manage. Also, solvent reclamation and reuse is much easier before solvents are mixed with other wastes. Some tips and tech-

niques for proper handling are described in Sections 2.2.3, "Toxic Air Emissions," and 3.8, "Maintenance, Cleaning, and Nonprocess Chemical Control." In general, the key is to avoid dumping solvents down the drain with other wastes.

- *Wastes from continuous processes:* Dumps of dye and chemical mixes sometimes occur in continuous textile operations such as slashing, preparation, continuous dyeing, printing, coating, and finishing. Pollution prevention techniques that can be used include equipment modification, maintenance procedures, housekeeping, waste capture, and segregation of concentrated wastes from the general waste streams.

### 2.1.2 Hard-To-Treat Wastes

Hard-to-treat wastes include those that are persistent, resist treatment, or interfere with the operation of waste treatment facilities. They often contain nonbiodegradable or inorganic materials. Biological processes that occur in waste treatment systems generally cannot remove or break down these wastes.

Hard-to-treat textile wastes include color, metals, phenols, certain surfactants, toxic organic compounds, pesticides, and phosphates. Color and metals originate primarily from dyeing or printing operations, although metals are sometimes found in other processes (see Section 2.2.5, "Metals"). Phosphates are used primarily in preparation and dyeing (see Section 3.5, "Chemical Alternatives"). Nonbiodegradable organic materials include certain surfactants (see Section 4.4, "Chemical Specialties") and solvents (see Section 2.2.3, "Toxic Air Emissions"). These materials can resist treatment, pass through standard activated sludge systems, and contribute to aquatic or air toxicity.

Another example of a hard-to-treat waste is pesticide residue that is present in wool-processing wastewater. Mickelson et al. (1) report that several different chemical pesticides are used to process wool. The degradability of each is given in Table 2-1. Information such as this, in combination with other relevant data (e.g., aquatic toxicity of the materials, their degradation products, the amount of material released during production), should be used as a guide in selecting the appropriate pesticide (1). For more information, see Section 4.12, "Finishing."

Achwal (2) reported that preservatives such as biocide additives in warp size materials can interfere with waste treatment system operation and can, in some cases, inhibit aerobic stabilization of wastewater. Some countries have banned the use of chlorinated phenols as a size additive. Undegraded size materials can cause biomass to aggregate (flock) and inhibit oxygen transfer. Starch can cause the growth of hard-to-settle filamentous bacteria, interfering with the operation of clarifiers. Synthetic sizes, mainly polyvinyl alcohol (PVA), do not

**Table 2-1. Degradability of Alternative Pesticides in Wastewater Treatment Systems (1)**

Pesticide	Percent Degraded
Dieldrin	81
Dichlorofenthion	79
Diazinon	87
Cyperethrin-1	84
Cyperethrin-2	90
Deltamethrin	92

cause these problems, nor are they toxic. Residues from other synthetic sizes, however (such as polyacrylic acid [PAA]), are also hard to treat and require tertiary treatment. For more information, see Section 4.7, "Slashing and Sizing."

Because of the difficulties involved in treating some of these wastes, efforts should be made to identify and eliminate their sources wherever possible. Several methods of prevention are particularly effective, including chemical or process substitution; improved process control and optimization; waste segregation, capture, and reuse/recycle; and improved employee work practices. Each method is discussed briefly below.

#### 2.1.2.1 Chemical or Process Substitution

Several strategies are appropriate for eliminating offending and hard-to-treat chemicals from a process, including:

- *Substituting other, easier-to-treat chemicals:* Example: Substituting linear alkylbenzene sulfonates for hard-to-treat alkylphenol (AP) in scouring eliminates waste system pass-through and aquatic toxicity (see Section 4.4, "Chemical Specialties").
- *Making physical process changes to avoid the need for chemicals:* Example: Pressure dyeing polyester eliminates the need for nonbiodegradable dye carriers such as 1,2,4 trichlorobenzene (see Section 4.10, "Dyeing").
- *Altering a product or raw material specification to avoid the need for chemicals:* Example: Finishing cotton knits mechanically at natural width and yield avoids the need for resins that contain formaldehyde, which can contribute to hazardous emissions (see Section 4.12, "Finishing").
- *Substituting another process:* Example: Pad-batch dyeing of fiber reactive dyes on cotton eliminates the need for hard-to-remove salt and reduces hard-to-treat color (see Section 4.10, "Dyeing").

### 2.1.2.2 Improved Process Control and Optimization

With an enhanced understanding of the complex chemistry of a particular process and the response of the process to variables that can be controlled, facilities often can reduce or eliminate hard-to-treat wastes from that process. A good example is the reduction of hard-to-treat color in wastewater. Sections 4.3, "Dyes," and 4.10, "Dyeing," describe how to reduce color by selecting dyes of high affinity and controlling bath ratio.

### 2.1.2.3 Waste Segregation, Capture, and Reuse/Recycle

In most cases, when a waste is mixed with other wastes, it loses much of its reuse potential and value. Rather than allowing them to become mixed with other wastes, hard-to-treat wastes should be captured in their concentrated forms, thereby facilitating their reuse. This practice is called "dry capture" regardless of the physical state of the waste material (i.e., solid, liquid, gas, or semisolid sludge). A good example is the use of centrifugal extraction to remove excess mothproofing treatment solution from wool substrate. The concentrated residue removed from the centrifuge is returned to the process, reducing the amount that ultimately reaches the environment (see Section 4.12, "Finishing"). Another example is the recovery of caustic from mercerizing operations (see Section 4.9, "Preparation").

### 2.1.2.4 Improved Employee Work Practices

Often, workers can reduce the amount of hard-to-treat chemicals (e.g., dye spillage that produces colored wastewater) that are wasted if they are made more aware of prevention measures. The three steps necessary to prevent wastes resulting from employee work practices are identification, training, and control:

1. **Identification:** Each chemical that is hard to treat should be identified to workers.
2. **Training:** Workers should receive training on handling these chemicals with minimal losses.
3. **Control:** Worker performance should be audited to ensure proper control of materials.

### 2.1.3 High- Volume Wastes

High-volume wastes in textiles include water (especially washwater from preparation and dyeing stages), alkaline wastes from preparation, salt, cutting room waste, knitting oils, and warp sizes. These wastes sometimes can be reduced by recycle or reuse as well as by process and equipment modifications. Several methods of reducing specific high-volume wastes are described in other sections:

- **Wafer:** Section 2.2.7, "Water Conservation"
- **Salt:** Section 2.2.2, "Discharge of Electrolytes"

- **Acids and alkali:** Various sections (e.g., Section 4.10, "Dyeing")
- **Warp sizes:** Section 4.7, "Slashing and Sizing"

In addition, cutting room waste is another major waste stream that can be reduced. Palmer (3) estimated that carpet waste amounts to 2 percent of an annual 900 million square yards of production, or 18 million square yards of waste per year (a value of \$100 million). Denim is another example. Approximately 800 million yards of denim are produced in the United States each year, at an average weight of 12 ounces per linear yard. Total denim production thus amounts to more than one-half billion pounds per year (4). Fabric utilization efficiency in cutting and sewing ranges from approximately 72 to 94 percent, and the efficiency for cutting denim is typically 84 percent or less. Cutting waste, therefore, represents approximately 16 percent of denim production, or approximately 100 million pounds annually. Proper design, planning, information, and communication are essential to managing this waste stream (4).

### 2.1.4 Hazardous or Toxic Wastes

Hazardous or toxic wastes are a subgroup of hard-to-treat wastes. Because hazardous wastes have such a substantial impact on the environment, they are discussed as a separate waste class. In textiles, hazardous or toxic wastes include materials such as metals, chlorinated solvents, nondegradable surfactants, and a few other nondegradable or volatile organic materials. These materials often are used for nonprocess applications, such as machine cleaning. Appropriate reduction strategies include conservation, substitution, process modification, and maintenance/housekeeping. Where source reduction is not possible, such wastes can often be recovered through recycling. When neither is feasible, however, proper management and disposal practices must be followed. Specific examples of hazardous wastes and the sections of this manual that address them include:

- **Air toxics:** See Section 2.2.3, "Toxic Air Emissions."
- **Metals:** See Section 2.2.5, "Metals."
- **Toxic organic materials:** See Sections 4.4, "Chemical Specialties," and 2.2.6, "Aquatic Toxicity."

See also Section 1.2.4, "Hazardous Waste."

## 2.2 Specific Wastes or Waste Problems

The preceding section discusses generic categories of wastes to identify the general characteristics of wastes that make them most amenable to pollution prevention. This section presents specific examples for these wastes that are often found in textile processes and typical pollution prevention strategies applicable for each.

The following sections discuss several specific waste problems facing the textile industry. The basis for targeting these difficulties for discussion is their importance as unsolved problems of the present or the near future. Each of the following represents a significant challenge to the textile industry because the industry now has (or soon will have) needs that traditional waste treatment approaches cannot meet. The specific pollution issues include:

- Color: Section 2.2.1
- Salt: Section 2.2.2
- Air toxics: Section 2.2.3
- *h-proved treatability of wastes*: Section 2.2.4
- Metals: Section 2.2.5
- Aquatic toxicity.- Section 2.2.6
- Water conservation: Section 2.2.7

These sections explain why traditional waste treatment techniques are (or will be) insufficient to address these waste issues and why pollution prevention is important and in many cases represents the only long-term alternative.

## 2.2.1 Color Residues in Dyeing Wastewater

Color in effluent from textile dyeing and printing operations is being increasingly regulated and is widely recognized as a compliance problem that must be addressed through pollution prevention (4-8). Effluent from most textile dyeing operations generally has a dark reddish-brown hue that is aesthetically displeasing when discharged to receiving waters. Although only an aesthetic pollutant,<sup>1</sup> color might be easy to detect (depending on the flow of the receiving stream), and even trace quantities of commercial textile colorants in wastewater are readily evident to the naked eye. Although many methods of color removal exist, none works in every case (9). Because of the difficulties and expense in treating color, the best approach for minimizing color discharges is pollution prevention (6).

### 2.2.1.1 Measuring Color

Measuring color in textile wastewater is inherently difficult (9). If the wastewater sample is not filtered, suspended solids can interfere with transmission measurement, rendering the measurement meaningless. If the sample is filtered, then the resulting measurement probably will not reflect the appearance of the wastewater because the turbidity will have been removed. Despite these acknowledged difficulties, the industry uses several color measurements, including:

- *Color*: Two methods are available for measuring color, based on American Dye Manufacturers Institute (ADMI) and American Public Health Association (APHA) protocols. Each method measures the color of light transmitted through a filtered wastewater sample, resulting in the computed value of a single number characterizing overall color.
- *Turbidity*: Turbidity is a measure of the light-scattering properties of the wastewater. Turbidity is calculated by comparing the intensity of light scattered by a sample compared with a reference suspension under the same conditions.
- *Apparent Color*: Apparent color is a measurement that attempts to combine the two measurements above (color and turbidity).

Because of the extremely high variability of tinctorial characteristics of dye solutions, generalizations cannot be made about the amount of dye (in percent or parts per million [ppm]) that will produce a specific color perception, or color value on the ADMI, APHA, or turbidity scale. In addition, many color regulations are written in qualitative language such as “no appreciable change in the color of the receiving waters” that provides mills with little guidance on permissible levels in the waste stream. Thus, color measurement is at best difficult, sometimes meaningless, and often bears little relation to regulatory and permit compliance language.

### 2.2.1.2 Sources of Color in Wastewater

Dyes and pigments from printing and dyeing operations are the principal sources of color in textile effluent. Dyes and pigments are highly colored materials used in relatively small quantities (a few percent or less of the weight of the substrate) to impart color to textile materials for aesthetic or functional purposes (10). In typical dyeing and printing processes, 50 to 100 percent of the color is fixed on the fiber (see Table 4-14), and the remainder is discarded in the form of spent dyebaths or in wastewater from subsequent textile-washing operations (8).

Reactive dyes are widely used and fall in the lower range of the fixation scale. As such, they require special attention to maximize fixation and therefore minimize waste color discharge. Important factors are bath ratio, optimized salt use, and adequate time for exhaustion. These issues are discussed in detail in Sections 4.3, “Dyes,” and 4.10, “Dyeing.”

Since the mid-1800s, dye chemists have attempted to meet consumer demand for color with outstanding permanence (i.e., color that is unaffected by cracking [rubbing], exposure to light, oxidizing or reducing agents, attack by chlorine or ozone, hydrolysis, or essentially any other environmental factor) (4). Their success has resulted in dyestuffs that have outstanding permanence

<sup>1</sup> Extremely high doses of color can interrupt photosynthesis in the receiving waters, producing impacts beyond the purely aesthetic. Most textile effluent, however, is not so severely colored.

and end-use qualities but are largely resistant to treatment or removal in wastewater treatment systems.

Three important ways of preventing and minimizing color discharges are:

- Maximizing exhaustion from dyebaths.
- Maximizing fixation and minimizing washoff.
- Optimizing dye handling to eliminate spillage, machine and implement cleanup, and discards.

### Maximizing Exhaustion From Dyebaths

To maximize dye exhaust, the dyer must understand the relationships between exhaust, affinity, and bath ratio, the three major dyeing process control parameters.\* Although these methods are discussed in much greater detail in Section 4.10, "Dyeing," the essential points are reviewed here as well.

Typical values for affinity, bath ratio, and exhaust are:

$$K \text{ (affinity)} = 50 \text{ to } 1,000 \text{ for various dye/fiber combinations}$$

$$L \text{ (bath ratio)} = 5 \text{ to } 50 \text{ for various machines (11)}$$

$$E \text{ (exhaustion)} = 0.50 \text{ to } 1.00 \text{ (50- to 100-percent exhaustion) (8)}$$

K (affinity) is a partition coefficient, or the ratio of the concentration of the dye in solution to the concentration of the dye in the substrate, at equilibrium, i.e.:

$$K = c^f / c^s \quad (\text{Eq. 2-1})$$

where:

$c^f$  = concentration of dye in fiber at equilibrium

$c^s$  = concentration of dye in solution at equilibrium

An important relationship is:

$$E = K/(K+L) \quad (\text{Eq. 2-2})$$

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

Affinity is an important factor in determining dye exhaust but one that resists generalizations. Each dye class is generally applicable to (or has affinity for) specific types of fibers. Individual dyes within dye classes, however, can show large variations in affinity. Therefore, "typical" exhaustion data provide only general guidelines. With these caveats in mind, typical exhaustion/fixation levels for various dye types are given in Table 2-2 (8).

\* This analysis applies only to dyes that do not react (including disperse, acid, and basic) or to reactive types during the exhaustion phase that precedes the beginning of the reaction.

**Table 2-2. Typical Exhaustion/Fixation Rates for Dyes of Various Classes (8)**

Dye Class	Typical K <sup>a</sup>	Typical Fixation (%)	Fibers Typically Applied to
Acid	130	80 to 93	Wool, nylon
Azoic	200	90 to 95	Cellulose
Basic	700	97 to 98	Acrylic
Direct	100	70 to 95	Cellulose
Disperse	120	80 to 92	Synthetic
Premets	470	95 to 98	Wool
Reactive	50	50 to 80	Cellulose
Sulfur	50	60 to 70	Cellulose
Vat	130	80 to 95	Cellulose

<sup>a</sup> The typical K is computed by assuming a bath ratio of 17:1 (typical for becks) and solving for  $K = EL / (1 - E)$ , where E is on a 0-to-1 scale. For acid dyes, the dye exhausted is typically 87 percent, or  $E = 0.87$ . Solving  $E = K/(K + L)$  for K results in  $K = L/(1 - E) = (17)/(0.13)$ , or 130. Therefore, at equilibrium, the concentration of dye in the fiber is 130 times greater than the concentration of dye in the bath for a dye that exhausts 87 percent at 17:1 bath ratio.

As seen in the table, cellulose dyes typically have poor exhaustion and fixation characteristics. The popular fiber reactive dye classes exhibit the poorest fixation. The same conclusions are reflected in Table 2-3, which shows wastewater color values from processes using different types of dyes (5). More recent data would no doubt show improvements in exhaust ratios for some dyes.

### Maximizing Fixation and Washoff

Fixation and afterwashing are important steps in dyeing and have substantial bearing on the levels of residual color in textile wastewater. Many methods are used for fixing dyes, including chemical insolubilization of the dye by oxidation or coupling (vat, sulfur, and naphthol dyes), chemical reaction of the dye with the fiber to form a covalent bond (fiber reactive dyes), reaction of the dye with the fiber to form an ionic bond (acid and basic dyes), formation of solid solution (disperse dyes), and the use of fixative agents (direct and fiber reactive dyes). These methods generally provide good fixation for most dye classes (acid, basic, disperse, direct, vat, sulfur, and naphthol). For fiber reactive dyes, however, fixation is often less than 75 percent. The problem of fiber reactive dyes is discussed in detail in Section 2.2.1.3.

Washing is an important step in determining final product quality and is discussed in greater detail in Section 2.2.7, "Water Conservation." Especially important for minimizing color carryover is the role of bath ratio in drop/fill wash procedures and the control of flow and mixing in overflow washing. Special methods such as countercurrent washing can also reduce color in addition to providing other benefits.

**Table 2-3. Wastewater Color Values Derived From Different Combinations of Dyes, Substrates, and Dyeing Equipment (5)**

Dye Number and Class	Substrate	Method	ADMI Color	ADMI Apparent Color
1 Vat	Cotton	Exhaust/Package	1,910	—
2 2:1 Premetallized	Polyamide	Exhaust/Beck	370	—
3 Disperse	Polyester	Atmospheric exhaust	315	—
4 After coppered direct	Cotton	Exhaust/Beck	525	1,280
5 Reactive	Cotton	Exhaust/Beck	3,890	—
6 Disperse	Polyamide carpet	Exhaust/Beck	100	—
7 Chrome	Wool	Exhaust/Beck	3,200	—
8 Basic	Polyacrylic	Exhaust/Beck	5,600	12,000
9 Disperse	Polyester carpet	Exhaust/Beck	215	315
10 Acid	Polyamide	Exhaust/Beck	4,000	—
11 Direct	Rayon	Exhaust/Beck	12,500	—
12 Developed	Rayon	Exhaust/Beck	2,730	—
13 Disperse/Acid/Basic	Polyamide carpet	Exhaust/Beck	210	720
14 Disperse	Polyester	High-temperature exhaust	1,245	—
15 Sulfur	Cotton	Continuous	450	—
16 Reactive	Cotton	Continuous	1,390	—
17 Vat/Disperse	Cotton/Polyester	Continuous	365	1,100
18 Basic	Polyester	Atmospheric exhaust	1,300	2,040
19 Disperse/Acid/Basic	Polyamide carpet	Continuous/Kuster	<50	190
20 Azoic	Cotton	Exhaust/Package	2,415	—

**Optimizing Dye Handling, Equipment Cleaning, and Housekeeping Techniques**

In addition to selecting dyes and dyeing methods that promote maximum dyebath exhaustion, proper work practices in the mix kitchen, cleaning operations, scheduling, and other factors are important for reducing effluent color. Best management practices for these aspects of textile operations are described fully in Sections 3.8, “Maintenance, Cleaning, Nonprocess Chemical Control,” 3.14, “Scheduling Dyeing Operations To Minimize Machine Cleaning,” and 4.18, “Support Work Areas.”

**2.2.1.3 Fiber Reactive Dyeing**

Poor fixation has been a longstanding problem with fiber reactive dyes (12), and batch dyeing with fiber reactive dyes represents perhaps the greatest challenge to the textile industry in terms of minimizing color discharge. Considerable research and development on this issue are now underway. Mill dyers must understand the fundamental principles behind fiber reactive dye fixation efficiency and their relationship to color discharges.

Typical fiber reactive batch dyeing processes include “two-step” and “all-in” processes. General procedures are shown in Table 2-4. In the two-step procedure, the dyeing process runs in a reversible exhaustion mode until alkali is added, at which time the dye starts reacting. Because the dye is more exhausted at the onset of the reaction, it is more likely to react with fiber. In the all-in process, no initial exhaustion occurs, and the entire dyeing process is a nonreversible, simultaneous

diffusion and first-order reaction. The all-in process results in lower percentage fixation and, therefore, more color in the wastewater.

Bireactive “double-anchor” dyes, which are now being promoted to reduce wastewater color even when applied by the two-step process, do not achieve the full expected fixation from the second reaction because

**Table 2-4. Comparison of Steps in Alternative Dyeing Procedures for Fiber Reactive Dyes**

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 to 45 minutes	Run 30 to 45 minutes
Hot patch decision	Hot patch decision
If okay, wash	If okay, wash
Cold patch decision	Cold patch decision
Drop bath and unload	Drop bath and unload

almost all the first-dye hydrolysis occurs in the solution. Therefore, the second reaction is always similar to the all-in process.

The key to high fixation (and 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.
- Achieving maximum exhaustion before adding alkali.
- Allowing sufficient time for full fixation.
- Using optimized temperature, salt, and alkali concentrations.

For some dyes, particularly “vinyl sulfone” types that react by the Michael addition mechanism, the activation energy for hydrolysis is not as great as the activation energy for the reaction with cellulose. Therefore (based on the Arrhenius equation), raising the temperature on these dyes causes hydrolysis to increase in rate faster than the reaction with cellulose, leading to more hydrolysis. The triazines, on the other hand, react by a nucleophilic substitution reaction (not addition) and thus have the same activation energy for water and for cellulose. As a result, temperature is not as significant in terms of color discharges.

### **Factors Affecting Fixation of Fiber Reactive Dyes**

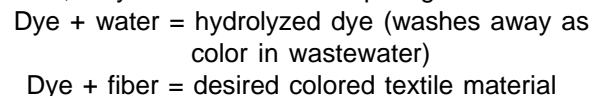
The fixation of fiber reactive dyes is influenced by many factors, including fiber shape, bath ratio, dye partition coefficient (affinity), and reaction rate constant. Although these factors interact in complex ways, evaluating the role of each parameter listed above is possible. The standard theoretical analysis is in terms of fixation efficiency (E), which should be maximized to reduce color in wastewater.

Fixation efficiency is an extremely complex, widely misunderstood subject. Theoretical models can be set up, but these models are based on primitive assumptions (e.g., infinite plane slab of substrate) to simplify the differential equations and boundary conditions. Even in simplified cases, the resulting differential equations sometimes cannot be easily solved. The problem of estimating fixation relates to simultaneous diffusion and first-order kinetics reactions (13). Despite these difficulties, equations and data verified by experiments show that three main factors are important. (A fourth factor, fiber shape, is also important, but is not controllable.)

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

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

Although many different kinds of fiber reactive dyes exist, they all involve two competing reactions:



Fixation efficiency is the ratio of the dye fixed (desired reaction) to the dye hydrolyzed (undesired reaction) (13). A fairly straightforward kinetic analysis leads to the following equation:

$$E = \frac{S}{L} \times \frac{[D_f]}{[D_s]} \times \sqrt{\frac{D}{K_H} \frac{R_f [CellO^-]}{[OH^-]}} \quad (\text{Eq. 2-3})$$

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 rate constant with cellulose to reaction rate constant with water, usually a constant approximately equal to 1
- $[CellO^-]/[OH^-]$  = ratio of ionization constants of cellulose to water, usually approximately 30:1 (cellulose ionizes approximately 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 versus log D (13) to be a constant multiplied by  $K^{1/2}$ . Based on this, and lumping all the constant (fixed) terms into one, the following relationship can be obtained:

$$\text{Efficiency of fixation} \cong (\text{A constant}) * (K^{1/3})/(k^{1/2}) \quad (\text{Eq. 2-4})$$

This relationship is shown in Figure 2-1.

### **Using Conventional Fixatives**

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

#### **2.2.1.4 Pollution Prevention Strategies**

A mill can take many actions to reduce color in wastewater. Each of these actions uses process optimization

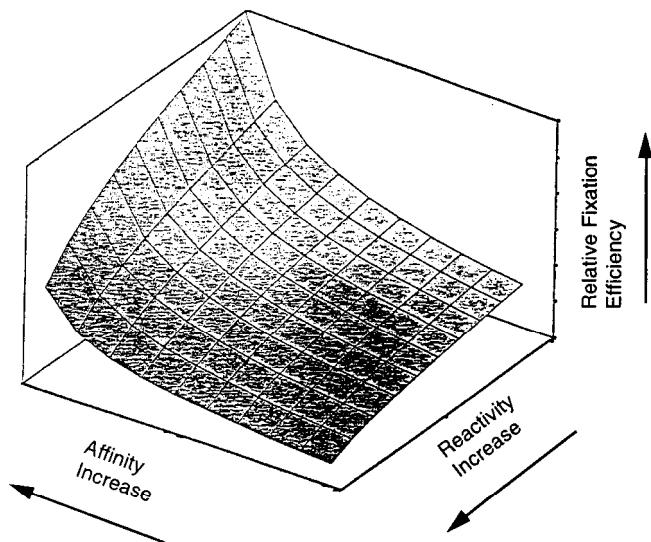


Figure 2-1. Relationship between affinity, reactivity, and fixation efficiency.

to achieve the highest possible fixation (8). The strategies for achieving high fixation vary depending on whether batch or continuous dyeing is performed because better fixation in batch dyeing is related to a combination of exhaustion and fixation, while in continuous dyeing it is usually related only to fixation.

### Batch Dyeing

Because of the high  $k$  values for dyeing of synthetic fibers and wool, the main problems with color in effluent result from cotton dyeing. In the general design of cellulosic batch dyeing processes, the most important factors are to:

- Ensure a good cloth preparation.
- Use a low bath ratio.
- Select high-affinity dyes.
- Optimize pH and salt, if used, for each recipe.
- Use proper time-temperature profile relationships.
- Avoid auxiliaries that retard or reduce exhaustion.
- Minimize the use of auxiliaries and surfactants.
- Avoid adding more chemicals (e.g., defoamers) to offset the undesired side effects of other chemicals in favor of nonchemical alternatives (e.g., procedural or mechanical remedies, or changing the dye selection or the product itself).

For fiber reactive dyes (the worst offender of poor fixation):

- Use two-step dyeing for fiber reactive, not all-in.
- Use fixatives for fiber reactive (as well as direct).
- Ensure maximum fixation by proper sequencing of events: (1) use high-affinity dyes and low-liquor ratio,

- (2) optimize factors such as salt and temperature for each recipe, (3) maximize dyebath exhaustion before adding alkali, and (4) use bireactive dyes.

### Continuous Dyeing/Printing

As in batch dyeing, the key to minimizing color discharges in continuous dyeing or printing operations is to maximize fixation, which occurs mainly through steam, thermofixation, or chemical agents. The proper dwell time and temperature in the steamer or thermofixation oven is essential. Also, the presence of air (oxygen) in steamers can oxidize vat dyes prematurely and lead to excessive washoff.

Also, making up only the amount of dye solution or print paste actually needed is equally important so that no extra solution or paste remains to be discarded at the end of the run. Discards and pad dumps are the main source of color in wastewater from continuous dyeing and printing.

Printing is an inherently messy operation, so housekeeping practices can have substantial bearing on overall color discharges. Paste handling and cleaning of mixers, homogenizers, screens, and squeegees should be closely controlled. Drums of print paste or "empty" drums of chemicals should not be washed out into the drain. Residues should be drained only into the next drum to be opened. If paste is left over (which it should not be), it should be reused or added to when making up a future (usually brown or black) color recipe. If using leftover paste in a future recipe is impossible, the paste should be scooped up, dried, and then landfilled as a solid material.

### Work Practices/Scheduling

The following work practices in the drug room or color kitchen are part of an effective pollution prevention strategy (11):

- Use of intermediate bulk containers, or IBCs.
- Dry capture (vacuum).
- Avoiding powder spills.
- Minimizing implement washup by using different dippers for each chemical or using automatic chemical dispensing.

### 2.2.2 Discharge of Electrolytes

Many types of salt are either used as raw materials or produced as by-products of neutralization or other reactions in textile wet processes (see Table 2-5). Several authors have identified salt in textile-dyeing wastewater as a significant future problem area (8). Typical cotton batch dyeing operations use quantities of salt that range from 20 percent to 80 percent of the weight of goods dyed, and the usual salt concentration in such wastewater is 2,000 ppm to 3,000 ppm (14). Regulatory limits imposed on textile facilities and on publicly owned treat-

**Table 2-5. Types of Salt Used in Textile Operations and Toxicity Characteristics**

Salt Type	Typical Use	Aquatic TLM <sub>96</sub> (ppm)	Typical Mammalian Oral Toxicity LD <sub>50</sub> (mg/kg) <sup>a</sup>
Calcium chloride	Formed	>1,000 <sup>a</sup>	3,500
Common salt	Dyeing	2,000 <sup>b</sup>	3,000
Epsom salt	Fixing	NA	3,000
Glaubers salt	Dyeing	NA	6,000
Magnesium chloride	Catalyst	NA	8,100
Potassium chloride	Formed	1,000 - 100 <sup>a</sup>	7,000

<sup>a</sup> From Sax (15)

<sup>b</sup> From Herlant (16).

ment facilities (POTWs) that receive textile wastewater start at 250 ppm (see Section 2.2.2.3).

The removal of salt from mixed textile wastewater to reduce chloride concentration from 3,000 ppm to 250 ppm is extremely difficult and expensive by any known treatment method. Therefore, reducing salt concentrations through pollution prevention measures is the only practical alternative to solve the dilemma presented by this hard-to-treat, toxic, high-volume waste.

This section considers mainly the chloride and sulfate salts of sodium, potassium, and magnesium. Certain specific organic anions and miscellaneous inorganic anions, as well as salts of the “heavy” metals, are discussed in more detail in other chapters. Common salt (sodium chloride) and Glaubers salt (sodium sulfate) constitute the overwhelming majority of total salt use. Other salts used as raw materials or formed in textile processes include Epsom salt (magnesium chloride), potassium chloride (from potassium hydroxide), and others in low concentrations. Although the mammalian and aquatic toxicities of these salts are very low, their massive use in certain textile-dyeing processes can produce wastewater that is well above the toxic limit.

### 2.2.2.1 Sources of Salt in Wastewater

The type and amount of salt used in dyeing processes is dictated by cost, corrosion considerations, the type of dyeing machine used, bath ratio, type of dye, and fiber being dyed. Common salt is the cheapest at about \$0.04 per pound compared with \$0.10 for Glaubers salt, but it is more corrosive to equipment and, therefore, some dyers prefer Glaubers salt. Also, Glaubers salt gives brighter shades with certain dyes.

In addition to the use of salt as a raw material, many reactions in textile wet processing produce salt as a by-product. In one case study (17), a moderate-sized mill, dyeing about 400,000 pounds per week of cotton knit fabrics, used substantial amounts of the major production acids and alkalis over a 6-week period. Quanti-

ties are shown in Table 2-6. These acids and alkalis ultimately reacted in the waste stream either with each other or with pH neutralization chemicals added in waste treatment to produce well over 50,000 pounds of salts plus a pH value of over 10 in about 200 million liters of water. Thus, the wastewater contained neutralization salts from just these top six acids and alkalis of about 60 ppm (17). In addition, many other chemical reactions that occur in textile processes produce salts. Table 2-7 lists some examples.

Many textile dyes and specialty chemicals also contain salt. Most notably, salt acts as a diluent in commercial dyes, and a typical direct or fiber reactive dye may actually be 20 to 70 percent salt.

### 2.2.2.2 Use of Salt in Dyeing Processes

Salt serves many functions in the dyeing process, and the literature has described its action in many ways. Generally, salt is used to assist the exhaustion of ionic

**Table 2-6. Typical Amounts of Salt Used or Generated in Textile Operations (17)**

Acid or Alkali	Amount (pounds)
Acetic acid	16,200
Caustic 35%	27,520
Caustic 50%	10,815
Soda ash	4,500
Sulfuric acid	2,854
TSP=	5,800

<sup>a</sup> TSP = trisodium phosphate.

**Table 2-7. Types of Salt Discharged From Various Process Sources**

Process Source	Type of Salt Introduced Into Wastewater
Diazotization of dyes	Sodium nitrate
Dyeing pH control	Ammonium sulfate, common salt, glaubers salt, acetate and formate salts
Incoming fiber	Common salt, other chlorides
Hypochlorite bleaching	Calcium chloride
Ion exchange filters	Glaubers salt, common salt
Process water from source	Common salt, calcium chloride, and magnesium chloride
Reduction clearing (hydro)	Sodium sulfate
Sodium chlorite stripping	Common salt
Triazine reactive dyeing	Common salt
Vat dye oxidation	Sodium iodide
Vinyl sulfone reactive dyeing	Glaubers salt
Water conditioning	TSPP <sup>a</sup>

<sup>a</sup> TSPP = tetrasodium phosphate.

dyes, particularly anionic dyes such as direct and fiber reactive dyes on cotton. Salt has many effects in the direct dyeing of cotton (13):

- Increases ionic strength of the dyebath
- Increases dye affinity for cellulose fiber
- Alters the dye diffusion coefficient
- Disrupts hydration of anionic dyes
- Disrupts hydration of cellulosic dye sites
- Increases potential for dye interactions (e.g., aggregation)
- Offsets fiber's negative zeta potential
- Provides electrical neutrality through counter/co-ions
- Salts out anionic dye by common ion effects

Figure 2-2 illustrates how salt addition can increase dyebath exhaustion. For Colour Index (CI) Direct Yellow 12, raising salt concentrations from 0.5 grams per liter to 4 grams per liter causes dyebath equilibrium exhaustion to increase by an order of magnitude (18).

### 2.2.2.3 Regulatory Status

The U.S. EPA has published national water quality criteria for chlorides, recommending that the 4-day average concentration of dissolved chloride (when associated with sodium) should not exceed 230 milligrams per liter more than once every 3 years and the 1-hour concentration should not exceed 860 milligrams per liter more than once every 3 years on average (19). States (or EPA) use this guidance to establish limits on a permit-by-permit basis through the National Pollutant Discharge Elimination System (NPDES). The federal criterion is for an instream concentration, so the limits on final effluent established in NPDES permits depend on

factors such as the discharge flow, stream classification, the size of the receiving water (instream waste concentration or dilution factor), and the number of dischargers. Depending on the factors listed above, textile mills typically must meet POTW pretreatment limits or NPDES chloride permit limits of 250 ppm and upward (20).

### 2.2.2.4 Pollution Prevention Practices for Salt Reduction

To reach new instream limits for chloride of 250 ppm, mills need to initiate significant pollution prevention efforts on several fronts (21). Salt is cheap and effective and has low toxicity. As a consequence, mills often misuse or overuse salt (21). Salt is also very versatile; thus, a major research breakthrough would likely be required to find another chemical that could perform all the functions of salt at comparable cost and with lower toxicity.

Despite the difficulties apparent in eliminating salt, several approaches to reducing salt, specifically from cotton dyeing, are available. These should be examined closely in light of tightening limits for chloride in textile effluent. The general principles to follow to minimize salt use are listed below, and several are discussed in more detail in the paragraphs that follow. Each principle entails tradeoffs that should be understood before implementing them as possible solutions:

- Use the lowest practical bath ratio in batch dyeing.
- Optimize salt use individually for each dyeing (as opposed to standard procedures used for all batches or runs).
- Consider continuous dyeing pad-batch dyeing process alternatives.
- Minimize discards and production color changes in continuous dyeing and printing.
- Design and make products from fibers other than cotton.
- Reuse batch dye baths.
- Ensure proper handling of dyes and fabrics.
- Select dyes that exhaust with minimum salt.
- Optimize dyeing temperature individually for each recipe.
- Inform fashion designers which colors and fabrics have high associated environmental loads (due to salt use) and work to find alternatives that avoid these impacts.

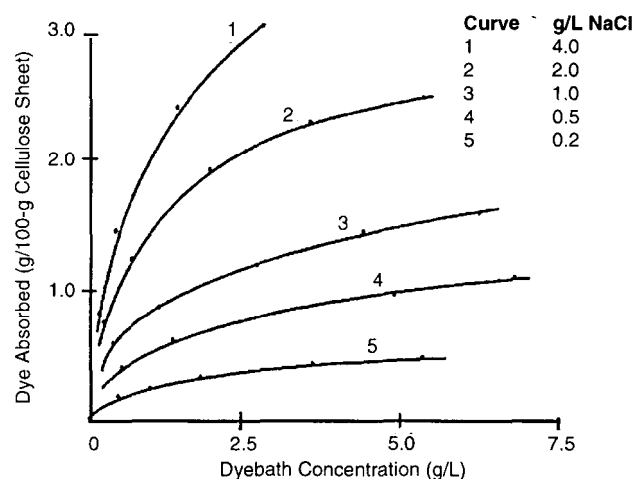


Figure 2-2. Adsorption isotherms of Chrysophenine G on cellulose sheet at 40°C and varying salt concentrations (see legend) (18).

### Low Bath Ratio

In recent years, machine manufacturers have tended toward lower bath ratio dyeing systems for energy conservation as well as chemical savings. Ultra low liquor ratio (ULLR) dyeing systems are discussed in detail in Sections 3.19, "Pollution Prevention Through New Equipment," and 4.10, "Dyeing."

Batch dyeing at low bath ratios in these machines conserves salt because salt use is based on the amount of dyebath present (owb), rather than the weight of the fiber or the goods (owf or owg).<sup>3</sup> The rule is: owb times the bath ratio equals owg. For example, in a 5:1 bath ratio ULLR dyeing machine, 50 grams per liter of salt is 25 percent owg, but at 40:1 bath ratio in a hosiery dyeing machine, the same 50 grams per liter salt is 200 percent owg. In each case, the salt is the same (i.e., 50 grams per liter owb). Types of dyeing machines vary greatly in their bath ratios, as shown in Table 2-8, which translates into different salt requirements.

**Table 2-8. Salt Requirements of Various Dyeing Machines (11)**

Machine	Bath Ratio	Salt Required (pounds) <sup>a</sup>
Garment	50	2,500
Paddle	40	2,000
Skein, beck	17	850
Jet, stock	12	600
Beam, package	10	500
Low bath jet	8	400
ULLR. iia	5	250

<sup>a</sup> Pounds of salt required per typical 1,000-pound production lot to produce 50 gal/L bath concentration.

Each of the above batch dyeing systems has its own limitations and range of applicability to particular substrates and styles. Continuous and pad-batch dyeing of fiber reactives on cotton can completely eliminate the need for salt, but certain other restrictions and limitations apply in terms of economics as well as the types of substrates that can be handled (22). The topic of pad-batch dyeing is fully reviewed in Section 4.10, "Dyeing." Continuous methods are discussed in Section 3.10, "Process Alternatives."

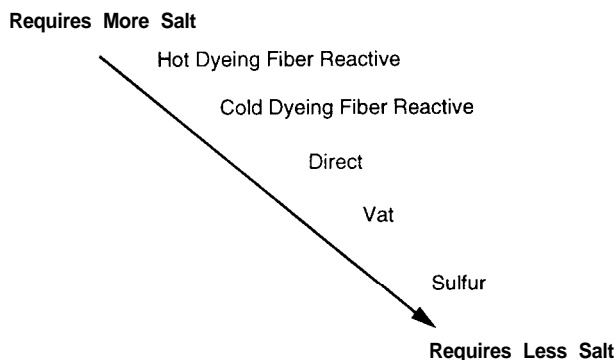
Individual manufacturers' batch dyeing machines vary slightly within the generalization above. All batch machines should be filled consistently to a fixed volume of dyebath, and the weight of goods loaded should be the same for each dyeing. Otherwise, the bath ratio will vary, leading to poor shade repeats and other problems. This may seem elementary, but dyehouses often do not specify the fill level for the machine and, therefore, do not fill machines consistently. Variable lot sizes are also encountered because of variation in customers order sizes. The net effect is an undesirable variation in bath ratio.

<sup>3</sup> Because salt has essentially no affinity for cellulose cotton fibers and therefore does not exhaust onto the fiber, the amount of salt should be computed based on the owb. Other dyebath components (e.g., dyes, softeners, lubricants) that do have definite affinity for the fiber, and therefore do exhaust, are always based owf or owg in batch dyeing processes.

The same types of consideration noted above apply not only to salt but also to all additives that act primarily on the bath (e.g., buffers, surfactants).

### Optimized Salt

Each dye class requires characteristic amounts of salt, and dyes within a class exhibit wide variances. In general, the salt requirements for batch dyeing of cotton with various dye classes are as shown in Figure 2-3 (7).



**Figure 2-3. Salt requirements for various dye classes—batch dyeing of cotton (7).**

Table 2-9 shows the amount of salt required to achieve 50-percent exhaust with a selection of direct dyes (18). Because of the variety in dye classes, no optimal amount of salt applies for all dyes and situations. Therefore, generalizations such as those shown in Table 2-10 may actu-

**Table 2-9. Salt Required to Produce 50-Percent Exhaustion of Direct Dyes (18)**

Dye	Salt Addition for 50% Exhaustion (% owf)
Chlorazol Brown MS	0
Benzopurpurine 10B	0
Benzopurpurine 4B	0.2
Chlorazol Dark Green PLS	0.4
Diazo Black OT	1.0
Melantherine BH	1.0
Chlorazol Green GS	1.2
Chlorazol Fast Yellow 5GKS	2.0
Oxyphenine GG	2.0
Primuline AS	2.0
Trisulphon Brown B	2.0
Chlorazol Fast Pink BKS	2.0
Diphenyl Brilliant Orange GR	4.0
Durazol Red 2BS	5.0
Benzo Fast Helio 4BL	4.5
Chlorazol Fast Eosine B	7.0
Benzo Fast Yellow RL	a.5
Benzo Fast Yellow 4GL	a.5
Chrysophenine G	13.0
Rosanthere Pink	16.0
Rosanthere Violet 5R	30.0

**Table 2-10. Typical Salt Application for Direct and Reactive Dyes on Cotton (18)**

Shade	Dye owf	Direct	Reactive
Pastel/Light	<1.5%	2.5-7.5 g/L	30-60 g/L
Medium	1.0-2.5%	7.5-12.5 g/L	70-80 g/L
Dark	>2.5	12.5-20.0 g/L	80-100 g/L

ally waste salt because recipes of some specific dyes may require significantly less salt. Each individual recipe should be optimized based upon controlled experimentation or analysis of production data. Typical salt-use practices for batch dyeing of cotton with direct and fiber reactive dyes are similar to those shown in Table 2-10 (16).

Another complication is that cost systems and computerized batch recipe programs often attempt to base all of the chemicals in the process owg. This is convenient from a cost accounting point of view but can lead to problems, for example, when the bath ratio varies due to fluctuations in lot size. If the salt is specified owg and the bath ratio varies, then the salt concentration owb will fluctuate, leading to poor shade repeats and environmental problems. A fixed amount of salt owg uses too much salt owb when bath ratio is low, or insufficient salt owb when bath ratio is high, leading to excessive color in the wastewater.

In response to the need to minimize salt, most major cotton dye manufacturers have active research and development programs to develop no- or low-salt exhaust dyeing systems. Hoechst Celanese has set a technical goal of reducing salt requirements to 25 grams per liter in the dyebath, while achieving dye fixation of 90 percent in exhaust dyeing of fiber reactive dyes (12). This is up to a 75-percent reduction compared with current commercial practice, which is to use up to 100 grams per liter of salt with fixation levels of 50 to 90 percent. The use of less salt generally provides lower exhaustion and, thus, more color pollution in wastewater.

### **Process Design**

A major control point for salt is product, process, and machine selection. Selecting alternatives that allow for reduced salt use can, however, involve tradeoffs. If batch dyeing of cotton is selected, then simply reducing salt concentration in the dyebath generally results in the negative environmental consequence of increased color in wastewater and also results in poor shade repeats. The classes that require the least salt (i.e., vat, sulfur, and naphthol) are more often used for continuous dyeing and are somewhat more difficult for batch dyeing than fiber reactive and direct types. In addition, the range of colors that can be produced with either vat, sulphur, or naphthol is more limited.

Finally, each dye class that allows for reduced salt use has its own particular problems, for example:

- *Fiber reactive* dyes: Massive salt requirements; color
- *Direct* color shade range and fastness properties.
- dyes: Offensive oxidizing/reducing agents re-
- *Sulfur* dyes: Sulfide in wastewater; limited shade range.
- *Naphthols*: Offensive organic compounds; limited shade range.

Each individual direct dye has a temperature of maximum affinity. Therefore, maximum exhaust with minimum salt occurs at a specific temperature (23). Few if any dyers actually set the final exhaustion temperature based on the optimum for a particular recipe, even though that is not difficult with modern microprocessor controllers. Table 2-11 gives optimum exhaust temperatures for over 100 direct dyes (23). Using these temperatures not only produces maximum exhaust with minimum salt use but also ensures consistent shade repeats and better quality.

### **Product Design**

Of course, fabric can be designed and produced from synthetic or woolen fibers, in which case salt use is very low or insignificant compared with batch dyeing of cotton. The tradeoff is the sacrifice of the comfort and aesthetics of cotton, plus the likely introduction of organic chemicals, dye carriers, levelers, and retarders required for other fibers. This may not be a viable option in all cases, but the important point is that fabric designers and fashion colorists should be made aware of the environmental loads associated with the selection of all types of fabrics and color ranges.

### **Handling**

Because of the low cost of salt, substantial amounts tend to be spilled, wasted, and washed down floor drains without much thought to the consequences. Although proper salt handling practices do not completely solve the problem, they should be addressed as part of a pollution prevention strategy. Storage of salt near high traffic areas or where water can spill on the bags fosters waste and should be avoided where possible. One of the best solutions to this problem is to use bulk salt systems or intermediate bulk containers (IBCs). Salt is readily available in IBCs, which are less susceptible to breakage during handling and which produce less packaging waste. Whenever salt or any other powder or granular chemical is spilled, it should be vacuumed up, not washed down the drain.

**Table 2-11. Maximum Affinity Temperature of Commercial Dyes (23)**

Dye Name	Chemical Type <sup>a</sup>	Commercially Available?	Molecular Weight	Maximum Affinity (°C)
<b>Yellows</b>				
Yellow 4	1, 5	Yes	624	—
Yellow 6	5	Yes	470	—
Yellow 7	4	—	591	—
Yellow 8	1, 4	Yes	530	—
Yellow 11	5	Yes	474	70
Yellow 12	1, 5	Yes	680	40
Yellow 19	1, 5	—	680	—
Yellow 20	1	—	554	—
Yellow 26	1	—	584	50
Yellow 27	1, 4	Yes	662	35
Yellow 28	1, 4	Yes	680	80
Yellow 29	1, 4	Yes	946	100
Yellow 44	1	Yes	634	50
Yellow 50	1	Yes	1,004	60
Yellow 106	5	Yes	—	95
<b>Oranges</b>				
Orange 1	1	—	642	50
Orange 8	1	Yes	635	70
Orange 15		Yes	416	80
Orange 26	1	Yes	804	80
Orange 29	1	Yes	870	80
Orange 34	1, 5	Yes	753	80
Orange 37	1, 5	Yes	783	100
Orange 39	1, 5	Yes	739	80
Orange 102	1	Yes	870	—
<b>Reds</b>				
Red 1	1	Yes	651	90
Red 2	1	Yes	772	80
Red 7	1	—	804	80
Red 10	1	—	745	80
Red 16	1	Yes	685	60
Red 17	1	—	745	50
Red 20	1, 4	—	657	60
Red 23	1	Yes	861	90
Red 24	1	Yes	950	100
Red 26	1	Yes	1,010	100
Red 28	1	Yes	744	80
Red 31	1	Yes	761	50
Red 32	1	—	—	—
Red 37	1	Yes	700	80
Red 39		Yes	728	80
Red 72	1	Yes	1,009	100
Red 75	1	Yes	1,038	80
Red 76	1, 5	Yes	813	100
Red 79	1	Yes	1,096	90
Red 80	1	Yes	1,420	100
Red 81	1	Yes	699	60
Red 83	1	Yes	1,068	100
Red 153	1	Yes	714	60
<b>Violets</b>				
Violet 1	1	Yes	776	100
Violet 9	1	Yes	715	40
Violet 22	1	—	848	—
Violet 47	1	Yes	1,048	90
Violet 48	1	Yes	979	100

**Table 2-11. Maximum Affinity Temperature of Commercial Dyes (23) (Continued)**

Dye Name	Chemical Type <sup>a</sup>	Commercially Available?	Molecular Weight	Maximum Affinity (°C)
Violet 51	1	Yes	743	40
Violet 66	1	Yes	951	—
<b>Blues</b>				
Blue 1	1	Yes	1,040	70
Blue 6	1	Yes	980	60
Blue 8	1	—	806	90
Blue 14	1	Yes	1,008	70
Blue 21	1	—	891	90
Blue 25	1	Yes	1,010	70
Blue 26	1	—	1,102	100
Blue 27	1	—	876	—
Blue 55	1	—	921	80
Blue 67	1	Yes	907	80
Blue 71	1	Yes	1,125	90
Blue 75	1	Yes	1,127	100
Blue 76	1	Yes	1,040	70
Blue 78	1	Yes	1,127	95
Blue 80	1	Yes	—	100
Blue 86	2	Yes	779.5	—
Blue 98	1	Yes	971	100
Blue 106	3	Yes	741	—
Blue 108	3	Yes	898	—
Blue 120	1	Yes	949	—
Blue 218	1	Yes	1,040	95
<b>Greens</b>				
Green 1	1	Yes	791	80
Green 6	1	Yes	836	80
Green 8	1	—	902	80
Green 11	1	—	788	60
Green 26	1	Yes	1,344	100
Green 28	1, 6	Yes	992	80
<b>Browns</b>				
Brown 1	1	Yes	680	100
Brown 2	1	Yes	651	70
Brown 6	1	—	682	100
Brown 25	1	—	991	90
Brown 29	1, 5	—	946	—
Brown 31	1	Yes	1,165	100
Brown 58	1	—	679	80
Brown 74	1	—	1,886	—
Brown 95	1	Yes	698	100
<b>Blacks</b>				
Black 3	1	—	567	100
Black 4	1	Yes	819	90
Black 9	1	Yes	816	100
Black 22	1	Yes	1,131	100
Black 38	1	—	805	—
Black 51	1	Yes	665	40
Black 56	1	—	947	80
Black 74	1	—	1,227	100
Black 80	1	Yes	978	90
Black 91	1	Yes	926	—
Black 166	1	Yes	—	—

<sup>a</sup> 1 = azo; 2 = phthalocyanine; 3 = dioxazine; 4 = thiazole; 5 = stilbene; 6 = anthraquinone.

## Batch Dye Bath Reuse

In some cases, batch dye baths can be reused, thus eliminating the need for additional salt except the small amount (about 10 percent) that is carried out with the wet dyed fabric. The subject of dyebath reuse is reviewed in Section 4.10, "Dyeing."

### 2.2.3 Toxic Air Emissions

Textile operations involve numerous sources of air emissions, and these sources give rise to a variety of air quality issues. Unit operations that present the greatest concern are coating, finishing, and dyeing (24). The textile industry is a relatively minor source of air pollutants compared with other industries, but the industry emits a great variety of materials, making sampling, analysis, treatment, and prevention more complex (25).

#### 2.2.3.1 Regulation

Air pollution from textile operations is not a new problem, but it has recently received increased attention. Title III of the 1990 Clean Air Act Amendments (CAAA) deals with air toxics, and will have a major impact on the textile industry. Title III identifies 189 hazardous air pollutants (HAPs) for which EPA is required to develop regulations (see Table 2-12). Specific HAPs emitted from textile processes, and their sources, are identified in Table 2-13. In addition to EPA, states also are developing regulations for air emissions. For example, the state of North Carolina has developed a list of 158 air pollutants to be regulated (26).

Because of emissions of nitrogen and sulfur oxides (NO<sub>x</sub> and SO<sub>x</sub>) from boilers, many textile plants are likely to be classified as "major sources" under Title III (i.e., sources that emit more than 25 combined tons per year of all listed HAPs). Although boiler emissions of NO<sub>x</sub> and SO<sub>x</sub> are the main sources of high-volume emissions, being classified as a major source will force textile plants to adopt controls for all emissions, including production and maintenance chemicals. The amounts of these materials emitted are low in most cases, however, and the economical approach is to reduce them as much as possible using pollution prevention practices.

Title III covers area sources of emissions as well as point sources. The CAAA's Maximum Achievable Control Technology (MACT) standards will likely require control technologies for the textile industry but the specifics of these technologies are still unknown. MACT is expected to include not only treatment measures but also pollution prevention measures such as chemical substitution, process changes, and capture of pollutants from processes, storage tanks, and fugitive sources. For some facilities, the expense of capture and treatment equipment will be immense.

Table 2-12. Initial List of 189 Hazardous Air Pollutants Identified in the Clean Air Act Amendments of 1990 (28)

No.	CAS <sup>a</sup> No.	Pollutant
1	75070	Acetaldehyde
2	60355	Acetamide
3	75058	Acetonitrile
4	98862	Acetophenone
5	53963	2-acetylaminofluorene
6	107028	Acrolein
7	79061	Acrylamide
8	79107	Acrylic acid
9	107131	Acrylonitrile
10	107051	Allyl chloride
11	92671	4-aminodiphenyl
12	62533	Aniline
13	90040	o-Anisidine
14	1332214	Asbestos
15	71432	Benzene (including benzene from gasoline)
16	92875	Benzidine
17	98077	Benzotrichloride
18	100447	Benzyl chloride
19	92524	Biphenyl
20	117817	Bis(2-ethylhexyl)phthalate (DEHP)
21	542881	Bis(chloromethyl)ether
22	75252	Bromoform
23	106990	1,3Butadiene
24	156627	Calcium cyanamide
25	105602	Caprolactam
26	133062	Captan
27	63252	Carbaryl
28	75150	Carbon disulfide
29	56235	Carbon tetrachloride
30	46358 1	Carbonyl sulfide
31	120809	Catechol
32	133904	Chloramben
33	57749	Chlordane
34	7782505	Chlorine
35	79118	Chloroacetic acid
36	532274	P-chloroacetophenone
37	108907	Chlorobenzene
38	510156	Chlorobenzilate
39	67663	Chloroform
40	107302	Chloromethyl methyl ether
41	126998	Chloroprene
42	1319773	CresoMCresylic acid (isomers and mixture)
43	95487	o-Cresol
44	108394	m-Cresol
45	106445	p-Cresol
46	98828	Cumene
47	94757	2,4-D, salts and esters
48	3547044	DDE
49	334883	Diazomethane
50	132649	Dibenzofurans
51	96128	1,2-Dibromo-3chloropropane

**Table 2-12. Initial List of 189 Hazardous Air Pollutants Identified in the Clean Air Act Amendments of 1990 (28) (Continued)**

No.	CAS <sup>a</sup> No.	Pollutant
52	84742	Dibutylphthalate
53	106467	1,4-Dichlorobenze(p)
54	91941	3,3-Dichlorobenzidene
55	111444	Dichloroethyl ether (Bis(2-chloroethyl)ether)
56	542756	1,3-Dichloropropene
57	62737	Dichlorvos
58	111422	Diethanolamine
59	121697	N,N-Diethyl aniline (N,N-Dimethylaniline)
60	64675	Diethyl sulfate
61	119904	3,3-Dimethoxybenzidine
62	60117	Dimethyl aminoazobenzene
63	119937	3,3'-Dimethyl benzidine
64	79447	Dimethyl carbamoyl chloride
65	68122	Dimethyl formamide
66	57147	1,1-Dimethyl hydrazine
67	131113	Dimethyl phthalate
68	77781	Dimethyl sulfate
69	534521	4,6-Dinitro-o-cresol, and salts
70	51285	2,4-Dinitrophenol
71	121142	2,4-Dinitrotoluene
72	123911	1,4-Dioxane (1,4-Diethyleneoxide)
73	122667	1,2-Diphenylhydrazine
74	106898	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
75	106887	1,2-Epoxybutane
76	140885	Ethyl acrylate
77	100414	Ethyl benzene
78	51796	Ethyl carbamate (urethane)
79	75003	Ethyl chloride (chloroethane)
80	106934	Ethylene dibromide (dibromoethane)
81	107062	Ethylene dichloride (1,2-Dichloroethane)
82	107211	Ethylene glycol
83	151564	Ethylene imine (aziridine)
84	75218	Ethylene oxide
85	96457	Ethylene thiourea
86	75343	Ethylidene chloride (1,1-Dichloroethane)
87	50000	Formaldehyde
88	76448	Heptachlor
89	118741	Hexachlorobenzene
90	87683	Hexachlorobutadiene
91	77474	Hexachlorocyclo-pentadiene
92	67721	Hexachloroethane
93	822060	Hexamethylene-1,6-diisocyanate
94	680319	Hexamethylphosphoramide
95	100543	Hexane
96	302012	Hydrazine
97	7647010	Hydrochloric acid
98	7664393	Hydrogen fluoride (hydrofluoric acid)
99	123319	Hydroquinone
100	78591	Isophorone
101	58899	Lindane (all isomers)

**Table 2-12. Initial List of 189 Hazardous Air Pollutants Identified in the Clean Air Act Amendments of 1990 (28) (Continued)**

No.	CAS <sup>a</sup> No.	Pollutant
102	108316	Maleic anhydride
103	67561	Methanol
104	72435	Methoxychlor
105	74839	Methyl bromide (bromomethane)
106	74873	Methyl chloride (chloromethane)
107	71556	Methyl chloroform (1,1,1-Trichloroethane)
108	78933	Methyl ethyl ketone (2-butanone)
109	60344	Methyl hydrazine
110	74884	Methyl iodide (iodomethane)
111	108101	Methyl isobutyl ketone (hexone)
112	624839	Methyl isocyanate
113	80626	Methyl methacrylate
114	1634044	Methyl tert butyl ether
115	101144	4,4-Methylene bis (2-chloroaniline)
116	75092	Methyl chloride (dichloromethane)
117	101688	Methylene diphenyl diisocyanate (MDI)
118	107779	4,4'-Methylenedianiline
119	91203	Naphthalene
120	98953	Nitrobenzene
121	92933	4-nitrobiphenyl
122	100027	4-nitrophenol
123	79469	2-nitropropane
124	684935	N-Nitroso-N-methylurea
125	62759	N-Nitrosodimethylamine
126	59892	N-Nitrosomorpholine
127	56382	Parathion
128	82688	Pentachloronitrobenzene (quintobenzene)
129	87865	Pentachlorophenol
130	108952	Phenol
131	106503	p-Phenylenediamine
132	75445	Phosgene
133	7803512	Phosphine
134	7723140	Phosphorus
135	85449	Phthalic anhydride
136	1336363	Polychlorinated biphenyls (aroclors)
137	1120714	1,3-Propane sultone
138	57578	beta-Propiolactone
139	123386	Propionaldehyde
140	114261	Propoxur (baygon)
141	78875	Propylene dichloride (1,2-Dichloropropane)
142	75569	Propylene oxide
143	75558	1,2-Propylenimine (2-methyl aziridine)
144	91225	Quinoline
145	106514	Quinone
146	100425	Styrene
147	96093	Styrene oxide
148	1746016	2,3,7,8-Tetrachloro-dibenzo-p-dioxin
149	79345	1,1,2,2-Tetrachloroethane
150	127184	Tetrachloroethylene (perchloroethylene)
151	7550450	Titanium tetrachloride
152	108883	Toluene

**Table 2-12. Initial List of 189 Hazardous Air Pollutants Identified in the Clean Air Act Amendments of 1990 (28) (Continued)**

No.	CAS <sup>a</sup> No.	Pollutant
153	95807	2,4-Toluene diamine
154	584849	2,4-Toluene diisocyanate
155	95534	o-Toluidine
156	8001352	Toxaphene (chlorinated camphene)
157	120821	1,2,4-Trichlorobenzene
158	79005	1,1,2-Trichloroethane
159	79016	Trichloroethylene
160	95954	2,4,5-Trichlorophenol
161	88062	2,4,6-Trichlorophenol
162	121448	Triethylamine
163	1582098	Trifluralin
164	540841	2,2,4-Trimethylpentane
165	108054	Vinyl acetate
166	593602	Vinyl bromide
167	75014	Vinyl chloride
168	75354	Vinylidene chloride (1,1-Dichloroethylene)
169	1330207	Xylenes (isomers and mixture)
170	95476	o-Xylenes
171	108383	m-Xylenes
172	106423	p-Xylenes
173		Antimony compounds
174		Arsenic compounds (inorganic including arsine)
175		Beryllium compounds
176		Cadmium compounds
177		Chromium compounds
178		Cobalt compounds
179		Coke oven emissions
180		Cyanide compounds <sup>b</sup>
181		Glycol ethers <sup>c</sup> 182
183		Manganese compounds
184		Mercury compounds
185		Fine mineral fibers <sup>d</sup>
186		Nickel compounds
187		Polycyclic organic matter <sup>e</sup>
188		Radionuclides (including radon) <sup>f</sup>
189		Selenium compounds

<sup>a</sup> CAS = Chemical Abstract Service.

<sup>b</sup> X'CN where X = H' or any other group where a formal dissociation may occur. For example, KCN or Ca(CN)<sub>2</sub>.

<sup>c</sup> Includes mono- and diethers or ethylene glycol, diethylene glycol, and triethylene glycol R-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-OR' where n = 1, 2, or 3

R = alkyl or aryl groups

R' = R, H, or groups that, when removed, yield glycol ethers with the structure R-(OCH<sub>2</sub>CH)<sub>n</sub>-OR. Polymers are excluded from the glycol category.

<sup>d</sup> Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral-derived fibers) of average diameter 1 micrometer or less.

<sup>e</sup> Includes organic compounds with more than one benzene ring that have a boiling point greater than or equal to 100°C.

<sup>f</sup> A type of atom that spontaneously undergoes radioactive decay.

Pollution prevention can be a viable low-cost alternative for accomplishing air quality improvement. In addition to

**Table 2-13. Hazardous Air Pollutants Found in Textile Plants (14)**

Chemical	CAS No.	Potential Source(s)
Acetic acid	64-19-7	Storage tank, dyeing machines, dryers
Ammonia	7664-41-7	Shop, storage tank
Chlorine	7782-50-5	Shop, water treatment
Ethylene oxide	75-21-8	Dryer stacks (wetting agents)
Formaldehyde	50-00-0	Bulk resin storage tanks, dryers, curing ovens, finished fabric warehouses
Hydrochloric acid	7647-01-0	Dryer stacks (catalyst)
Methylene chloride	75-09-0	Shop, paint stripper, etc.
Perchloroethylene	127-18-4	Dry cleaner, scour, carrier
Tetrachloroethane	79-34-5	Shop, inspection (spot remover)
Trichloroethylene	79-01-4	Shop, inspection (spot remover)
Toluene	108-88-3	Becks, dryers (carrier/scour)
Xylene	1330-20-7	Becks, dryers (carrier/scour)

being covered under Standard Industry Classification (SIC) 22, Textiles, fabric coating operations (some of the major HAP emitters) and surface finishers are tentatively covered under Surface Coating Processes (27).

### 2.2.3.2 Air Pollutants

Only recently have reliable data been collected regarding air toxics emissions from textile operations. As late as 1990, most estimates of air emissions from manufacturing operations were calculated using mass balance techniques rather than direct measurements (19). The mass balance technique often is not reliable because of the large quantities of input raw materials and output products. Using the difference between large input and output values to estimate the quantity of waste streams can lead to uncertain results (29).

Early attempts during the 1980s to measure air pollutants from textile operations were made using infrared transmission analysis (25, 30). This method proved to be a useful starting point, but it was unsatisfactory as a primary means for quantifying air pollution. The original Superfund Amendments and Reauthorization Act (SARA) Title III inventories of the early to mid-1980s also were a particularly poor source of air pollutant data. In most cases, the data were inaccurate, and groups with little knowledge of textile operations publicized the lists, leading to publication of data that were seriously flawed (26).

Several investigators have noted air pollutants that are of concern in textiles, including volatile organic compounds (VOCs), photoreactives (PRs), toxic air pollutants (TAPs), and HAPs (11, 25, 31, 32). As shown below, most of these pollutants subsequently have been de-

tected in air emission testing of textile operations. Since the 1980s direct reading tubes (DRAGER tubes) and gas chromatographs/mass spectrographs (GCs/MSs) have provided more reliable data (31, 33-35).

### 2.2.3.3 Sources

The main sources of air emissions in textile operations are:

- Boilers
- Machine and equipment cleaning:
  - General cleaners
  - Specific implements and parts cleaners
  - Screen-printing cleaners
- Processing machines:
  - Ovens, for drying and curing
  - Solvent processing units (e.g., dry cleaning)
  - Dyeing machines
  - Mix kitchens, drug rooms
  - Warehousing for finished cloth and chemical drums
- Storage tanks (breathing losses)
- Wastewater treatment systems

In addition to boilers, high-temperature finishing, drying, and condensation machines also emit many air pollutants. Hydrocarbons are emitted from drying ovens and, in particular, from mineral oil from high-temperature (200°C) drying/curing (35). These processes can emit formaldehyde, acids, softeners, and other volatile compounds. Residues of fiber preparations and their oxidation products sometimes form "blue haze" in heatsetting processes. Carriers and solvents used in dyeing and coating machines cause exhaust air pollution (36).

Textile manufacturing can produce oil and acid fumes (especially from the tenter frame), plasticizers, and other materials that can volatilize. Carbonizing of wool produces acids. Acetic acid emissions derive mostly from storage tanks, especially from vents during filling, and breathing losses (14, 36). The carbonizing process emits sulfuric acid fumes and decating produces formic acid fumes (37).

Dyeing and finishing operations can emit solvent vapors containing toxic compounds. These vapors might include acetaldehyde, chlorofluorocarbons, p-dichlorobenzene, ethylacetate, chlorobenzene, hexane, styrene, and others. Acetic acid and formaldehyde are two major emissions of concern in textiles. Some process chemicals exhaust into the fibers and are later evolved from dryers as VOCs; these chemicals include methyl naphthalene, chlorotoluene, trichlorobenzene, orthodichlorobenzene, perchloroethylene, methyl ester or cresotinic acid, butyl benzoate, and biphenyl (36). For-

maldehyde might be emitted from bulk resin storage tanks, finished fabric warehouses, driers, and curing ovens.

Many types of cleaning and scouring operations are used in textile operations, both batch and continuous. Perchloroethylene is used for solvent scouring operations, and CFC-113, 1,1,1-trichloroethane, and trichloroethylene are used to a lesser extent (38). These materials also are used as solvents during application of water-repellent finishes and for machine cleaning. In the aggregate, cleaning and scouring chemicals were estimated at 10,500 metric tons in 1988 (38).

Quality control (QC) inspectors in fabric and garment manufacturing operations use solvent/air guns to remove spots that originate from sewing machines that sling oil during high-speed seam sewing. The proper pollution prevention strategy in such cases is to eliminate the oil spots by modifying the sewing operation to prevent oil slinging, which reduces the need for spotting and cutting, as well as solvents, and also minimizes labor requirements while improving quality.

Odors often are associated with oil or solvent vapors and are usually removed by eliminating the source of the odor. A common odor problem in textiles is carrier odors from aqueous polyester dyeing and subsequent processing. Resin finishing also produces formaldehyde odor. In addition, odor problems are associated with sulfur dyeing on cotton and cotton blends, reducing or stripping dyes with hydrosulfite, bonding, laminating, back coating, and bleaching with chlorine dioxide (36).

Dust and fly are produced during processing of natural fibers and synthetic staple, before and during spinning, and by napping and carpet shearing. Most textile processes produce lint, which is not measured as a pollutant but causes other difficulties (36). Lint can clog filters and screens, causing them to malfunction. Lint can also foul sensors in the air handling equipment and interfere with incineration units. It collects in the ducts and stacks, eventually becoming an extreme fire hazard.

### 2.2.3.4 Printing

In the past, printing operations used solvent-based print pastes in which an oil-water emulsion provided the appropriate rheology. These pastes have been replaced almost completely by polymeric thickeners, which produce essentially no airborne pollutants. A few printers, however, still use the oil-water emulsion systems as thickeners. A small number of specialty print shops also still use solvent-based printing inks. A major source of solvent emissions in screen printing operations is cleaning of machines, screens, and squeegees. In one plant, GC mass spectrometric analysis showed the presence of the following VOCs (39):

- Trimethylcyclohexane

- Propylcyclohexane
- Hexylcyclohexane
- Ethylcyclohexane
- Methylethylcyclohexane
- Butylcyclohexane
- Decahydronaphthalene
- Butylethylcyclopentane
- Methyldecane (three isomers)
- Xylene (three isomers)
- Ethylbenzene
- Trimethylbenzene (three isomers)
- Methylethylbenzene
- Other hydrocarbons

Urea is emitted from the curing of fiber reactive prints and thermofix continuous dyeing of reactivities. Much emphasis has been placed on eliminating urea from print paste formulations because of problems with nitrogen nutrients discharged in wastewater. (See Section 4.11.4.11 for a discussion of urea and printing.)

### 2.2.3.5 Pollution Prevention Procedures

Many practical pollution prevention methods are available to reduce toxic air emissions. These methods are far-ranging and extend from optimization of boiler operation to redesign of products that produce fewer air toxics. Traditional air pollution control methods relied on end-of-stack add-on technologies to scrub or capture pollutants in the air stream. These technologies often are capital-intensive and usually have high operating costs. Pollution prevention methods often can achieve significant reductions in pollution with little capital expense.

The main pollution prevention methods for reducing air emissions are to:

- Design and manufacture products that do not produce HAPs.
- Identify sources and quantify emissions.
- Optimize boiler operations.
- Prescreen chemicals using material safety data sheets (MSDSs).
- Prescreen fibers for volatile spin finish components.
- Trap bulk storage tanks.
- Minimize or eliminate chemical auxiliaries in aqueous processes.
- Improve solvent processing operations.
- Avoid spills in bulk chemical off-loading areas.

- Investigate emerging technologies.

### ***Design Products That Do Not Produce HAPs***

Often, decisions made at the design stage significantly affect the manufacturer's decision to use products that contain VOCs, PRs, TAPs, and HAPs. These pollutants result from the use of processing specialties required to meet designer specifications. Usually, the designer has no knowledge or expertise in the pollution consequences of design decisions. The need to communicate this information, as well as the specific nature of the air issues involved, are reviewed in detail in other sections. (See Sections 3.2.2.1 and 3.2.2.2 for product design and Sections 1.2.1.1 through 1.2.1.5 and 2.2.3.1 through 2.2.3.5 for air pollutant issues.)

To summarize, the first step is to identify and communicate problem areas, especially which colors, styles, and fiber blends will produce air problems. Boiler emissions are the main air pollutant from textile mills, so products requiring low energy for production (and thus less steam and electricity) are preferred because they produce less air pollution. In addition, products with a high percentage of right-first-time performance are generally better in all pollution categories including air. Marketing decisions can also strongly influence pollution. For example, short runs, frequent style or color changeovers, and scheduling are also important, as discussed in Chapter 6.

Some specific examples of design issues include:

- The tendency to use hydrocarbon softeners instead of designing inherently soft fabrics. Softeners contain hydrocarbons that are emitted from drying ovens. In particular, mineral oil is emitted from high-temperature drying/curing (35).
- Printing of fiber reactive dyes using urea, which is emitted during the curing of fiber reactive prints and thermofix continuous dyeing of reactivities. Design alternatives include the use of alternative colors (which can be produced with colorants other than fiber reactive) or adjustment of product fastness requirements to allow for pigment printing.
- The use of soil-release finishes (which are often solvent-based finishes) as opposed to selecting inherently soil-releasing fibers such as cotton.
- The use of water repellent finishes (which are often solvent-based finishes) as opposed to selecting inherently water repellent soil-releasing fibers, such as polyester or wool, and inherently water repellent fabric constructions.
- The use of polyester and other fibers that contain volatile spin finishes that volatilize during heatsetting, as opposed to natural fibers that contain no spin finish and do not require heatsetting. This eliminates

not only the spin finish air pollution but also the burner emissions required for the heatsetting oven.

### **Identify Sources and Quantify Emissions**

Identifying sources and quantifying emissions are the first steps in pollution prevention (40). Potential sources can be identified by reviewing MSDSs for each chemical in the facility (41). Once identified, potential sources can be quantified by continuous emissions monitors and by applying emission factors or preparing mass balance calculations (40).

Point sources are the easiest to identify and monitor. Fugitive or area sources are more difficult to identify and quantify because of problems often encountered when measuring flow rates and concentrations. Because of the wide variety of sources and processes, the textile industry has been described as one of the most difficult in which to establish a good pollution prevention program for air emissions (40).

### **Optimize Boiler Operations**

Boilers are a main source of hazardous emissions, including NO<sub>x</sub> and SO<sub>x</sub>. Improperly operated boilers can contribute excess amounts of such pollutants. Careful optimization of boiler operations is necessary to minimize air emissions.

### **Prescreen Chemicals Using MSDSs**

As described further in Sections 3.7, "Incoming Raw Material Quality Control," and 3.12, "Raw Material Prescreening Before Use," best management practices for pollution prevention include a comprehensive program to prescreen all chemicals. Prescreening can start by first consulting the MSDSs. For air emissions, shop chemicals should receive special attention. Chemical inventory managers should seek maintenance and process chemicals that will not contribute to air emissions (i.e., nonvolatile, nonhalogenated, and nonphotoreactive chemicals and those not on the list of TAPs or HAPs).

### **Prescreen Fibers for Volatile Finishes**

Incoming QC also can be performed on synthetic fibers to identify spin finishes with components that could vaporize during heatsetting. One method of prescreening is to heat the fabric (or yarn) in a laboratory oven and observe or sample the air from the oven vent. Sampling can be performed using various methods described in the literature (25, 30, 32, 34, 40).

### **Trap Bulk Storage Tanks**

Storage tanks can be equipped with carbon canisters on vents to remove fugitive vapors. The carbon canisters must be maintained on a regular basis to effectively trap such vapors. Filling systems also must be designed and maintained to prevent spills and vapor losses during operation.

### **Minimize or Eliminate Chemical Auxiliaries**

Use of pressure dyeing at 250°F to 265°F for polyester can eliminate the need for dye carriers. Mills should seek to reduce the use of dyeing auxiliaries in general, paying particular attention to those used for synthetics. Alternative methods are shown in Table 2-14.

**Table 2-14. Nonchemical Methods To Assist in Eliminating Dyeing Auxiliaries**

<b>Fiber Type</b>	<b>Dyeing Assistants To Target</b>	<b>Alternative Methods of Control</b>
Acrylic	Retarder	Rate of temperature rise
Nylon	Retarder	pH, temperature
Nylon	Leveller	pH, temperature
Polyester	Carrier	Temperature, time
Polyester/Cotton	Lubricant	Fabric transport mechanism

A considerable amount of information on alternative methods is included in Section 4.10, "Dyeing."

### **Improve Solvent Processing Operations**

Solvents that pose hazards (PRs, HAPs, or TAPs) ideally should be replaced with nonsolvent systems (i.e., aqueous or mechanical/physical). In cases where replacement is not possible, other procedures can be undertaken:

- Review solvent selection to ensure use of the least offensive, least volatile solvent. Nonhalogenated solvents are generally preferable. Chlorinated solvents can be substituted with deodorized kerosene, hexane, or Stoddard solvent (38).
- Implement special practices for monitoring solvent losses from textile operations (38, 40). Careful records should be maintained to accurately estimate losses to the air. Solvent losses should be monitored during special events in the process (e.g., startup, shutdown, changeover).
- Dispense solvents directly from bulk container to machine; do not carry solvents in secondary containers. Submerge fill pipes to avoid splashing, which increases air/solvent contact (38).
- Purchase, or design and use, application-specific solvent-use devices (e.g., for parts cleaning) (11).
- Plan and document routine maintenance for solvent-use operations.
- Pay special attention to scheduling on solvent-use processes to reduce start/stop/change losses.
- Reclaim and reuse solvents, either on site or off site. A QC program for solvents is important because it helps

detect decomposition of solvents during processing or buildup of contaminants that can render the process less effective or inhibit reclamation of the solvents (38).

Maximize capture efficiencies for solvent vapors from processes (e.g., coated fabrics for offset printing blankets) by proper design of containers, mix areas, dryers, etc. In some cases, mills have spent more than \$1 million on reclamation equipment (e.g., carbon sorption, distillation) only to find that air pollution is still a problem because of poor capture efficiencies.

Focus on worker training to ensure proper handling of materials, limiting their release to the atmosphere (38). Train operators to look for leaks and potential spill points.

Maintain solvent recovery equipment in top working order. Batch distillation units generally range from as low as 60 percent for inefficient units or difficult solvents to 95 percent for efficient units (38).

### **Avoid Spills in Off-Loading Areas**

Chemical spills frequently occur in off-loading areas. Avoiding these fugitive sources of air pollutants is a matter of proper procedures, work practices, worker training, and facility design. Offloading areas should be well lit and easily accessible with ample work space so that the area remains orderly even when in full use. The base or floor should be non-absorbent and should have drainage and spill control features built in. One good system often seen in bulk tank areas is gravel with an underlying concrete drain system. Drains in off-loading areas should flow to appropriate treatment or collection areas, not to the storm sewer. If the area has a solid floor, it should be smooth, well sealed, and have good drainage (to avoid standing water or spilled liquids), which facilitates cleanup. A vacuum should be available for capturing powder spills, rather than washing them down the drain with water from a hose.

Drums and bags of chemicals should not be stored in standing water or over floor drains. Spill containment pallets are available that help prevent small-scale spills when off-loading drum chemicals. Bulk delivery hoses should have automatic shutoff valves and should receive careful attention so that, in case of failure, the delivery pump will shut down.

All receiving areas (bulk and warehouse) should be clearly labeled because outside personnel (truck drivers) may not be familiar with the area. Two people should be present at all times during off-loading of chemicals. Proper spill control equipment and training are required. Deliveries should take place during daytime hours so that proper procedures can be observed and so that help will be available in case of an incident.

Used drums being returned should not be washed on site, and residues should not be disposed of down the drain. Direct returnable IBCs should be used instead. If drums are used instead of IBCs, used drums should be emptied or drained thoroughly into new drums.

Proper equipment and good preventative maintenance in off-loading areas are essential, especially in bulk storage areas. Use of automatic bulk chemical systems helps control pollution, but the potential for large-scale spills is significant, especially during off-loading.

### **Investigate Emerging Technologies**

Technologies under examination for the future are supercritical fluid scouring and dyeing. These technologies use high-pressure carbon dioxide as a solvent. When the scouring or dyeing process is finished, no solvent residues remain to be vaporized and no energy is consumed in drying. Conventional disperse dyes on polyester can be used. Off-the-shelf laboratory-scale equipment already is available, and major equipment manufacturers show some interesting products at the International Textile Machinery exhibit each year.

### **2.2.4 Improving Treatability**

Properly designed waste treatment systems can remove or destroy many of the harmful contaminants in raw textile wastewater and produce an effluent that can be discharged safely to receiving waters. Certain wastes or contaminants, however, can interfere with the ability of treatment systems to operate to design specifications, resulting in system upsets and exceedences of permit limitations. Other contaminants are removed from the treatment system and partition into sludges, disposal of which can be difficult. Where possible, steps should be taken to avoid these wastes or to improve their treatability so that wastewater treatment systems can manage them more easily.

Prominent among these wastes are the four types that are amenable to pollution prevention (11, 42). These wastes, and the treatment problems they may pose, include:

<b>Waste Type</b>	<b>Problems</b>
Hard-to-treat	Pass through interfere with systems
Dispersible	Hard to collect or capture for treatment
Offensive	Inhibit treatment system operation Produce hazardous sludges
High volume	Increase loading Cause shock loads if intermittent

The sections below describe treatment problems posed by these wastes and recommend strategies for either improving their treatability or reducing the amounts of waste generated.

Several characteristic problems that arise from the presence of hard-to-treat waste in textile waste treatment systems include:

- Respiratory inhibition
- Bulking, poor settleability
- Sludge contamination
- Shock loading
- Pass-through of nondegradable materials

These effects can be quantified by several methods. Moore suggested a system for treatability evaluation (including inhibition), which includes results of Organization for Economic Cooperation and Development (OECD) tests for biodegradability (301 D), biomass impact (209), and aquatic toxicity (202).<sup>4</sup> Cooper reported an alternate system in which chemicals are ranked on a scale of 1 to 5 according to treatability using chemical oxygen demand to biological oxygen demand (COD:BOD) ratios (6).

Pollution prevention is a useful way to reduce treatment problems arising from these wastes. Wood and Bishop reported a highly successful pollution prevention program at DuPont to reduce hydraulic load, organic load (BOD), total suspended solids (TSS), methylene chloride, chloroform, and toluene (43). By reducing priority pollutants at the source and eliminating shock loads, wastes that interfered with treatment system operation were reduced, with a corresponding reduction in the incidence of permit violations (43). For more information, see Section 2.1.2, "Hard to Treat Wastes," and other sections mentioned below.

#### 2.2.4.1 Respiratory Inhibition

Many types of materials inhibit the action of biological waste treatment systems. The specific causes vary, but the symptoms are generally the same: low specific oxygen uptake and low BOD removal efficiency. The pollution prevention strategy is to seek out and control materials that are toxic to the biomass. These include:

- Metals
- Chlorinated organics
- Biocides

Biocides comprise not only those materials used around the wet processing plant but also preservatives (biocide additives) in warp size materials. These can interfere with the operation of the waste treatment system and can inhibit aerobic stabilization of wastewater (2). Some countries have banned use of chlorinated phenol

biocides as a size additive (2). For more information, see Section 4.7, "Slashing and Sizing."

#### 2.2.4.2 Bulking and Poor Settleability

Some textile chemicals tend to form suspended solids that neither settle nor float. These are usually neutral, buoyant solids or materials with a large, hydrodynamic radius and derive from specific sources, such as:

- Foam waste from coating, dyeing, and finishing.
- Acrylic sizes and handbuilders, which coagulate and trap air.
- Print pastes based on acrylic materials as above.
- Resins, N-methylol film formers that coagulate with lint.
- Size materials, such as gums and synthetic sizes.

Many of these wastes result from printing, finishing, and continuous dyeing. Methods of controlling them are based primarily on reducing or eliminating discards. This is described in Sections 4.11, "Printing," and 4.12, "Finishing."

Undegraded size materials can cause biomass to aggregate (flock) and inhibit oxygen transfer (2). Starch, in some cases, causes growth of hard-to-settle filamentous bacteria that interfere with the operation of clarifiers (2). Polyvinyl alcohol (PVA) does not cause these problems, nor is it toxic. Polyacrylic acid (PAA) is hard to treat and requires tertiary treatment (2).

#### 2.2.4.3 Sludge Contamination

Occasionally, textile wastewater treatment sludges are rendered hazardous because of accumulation of offensive materials in the sludge. Some common causes are:

- Metals
- Surfactants
- Chlorinated organics

Modak lists several materials of concern that fall into the above categories, such as chromium, copper, nickel, zinc, isocyanates, heavy metals, chlorinated organics, dioxins, mercury, cadmium, lead, pesticides (notably pentachlorophenol from wool finishing), and adsorbable organic halogens (AOX) (44). Richardson adds metals, solvents, surfactants, and quaternary amines (quats) to the list (21). Quats are used for processes such as disinfecting, scouring and softening (21).

In some cases, these materials can be readily identified from MSDS information (21). Special handling and use procedures for such materials (e.g., special training) are beneficial. Chemical substitutions should be investigated and implemented where possible. For further information on pollution prevention strategies, see

<sup>4</sup>Moore, S., and Smith, B. 1994. Personal communication between Samuel Moore, Burlington Research, and Brent Smith, Department of Textile Chemistry, North Carolina State University, Raleigh, NC.

Sections 2.2.3, "Toxic Air Emissions," 2.2.5, "Metals," and 2.2.6, "Aquatic Toxicity."

#### 2.2.4.4 Shock Loading

Shock loadings occur when waste characteristics change rapidly and upset waste system operations (21). In textile batch operations, discharged processing baths, cleaning chemicals, and excess chemical mix disposal can create extreme short-term variations in properties, as indicated in Table 2-15.

**Table 2-15. Typical Short-Term Variations in Processing Bath Parameters**

Property	Extremes	
	High	Low
Temperature	≥210°F	75°F
pH	11+	3
Salt concentration	120 g/L	0 g/L
BOD	100,000 ppm	0 ppm
Redox	Strongly oxidizing	Strongly reducing

Equalization is required to eliminate these variations. Even so, several pollution prevention approaches can help. As discussed in several other sections, the use of chemical equipment cleaners can be minimized by proper process and equipment design, chemical selection, and scheduling. The need to dispose of obsolete chemicals can be avoided by proper auditing, handling, and prescreening protocol. Obsolete chemicals should never be disposed of down the drain. Finally, process alternatives can make the properties of processing baths less extreme. If a bath or waste stream has extreme properties, it may well have some direct reuse value if segregated.

#### 2.2.4.5 Pass-Through of Nondegradable Materials

Many materials discharged from textile operations are not degradable in typical secondary activated sludge waste treatment systems. These include:

- Salt (see Section 2.2.2, "Discharge of Electrolytes").
- Chloro-organics (see Sections 2.2.3, "Toxic Air Emissions," and 4.12, "Finishing").
- Solvents (see Sections 2.2.3, "Toxic Air Emissions," and 4.12, "Finishing").
- Phosphates (see Section 3.5, "Chemical Alternatives").
- Color (see Sections 2.2.1, "Color Residues in Dyeing Wastewater," 4.3, "Dyes," and 4.10, "Dyeing").
- Surfactants (see Sections 2.2.6, "Aquatic Toxicity," and 4.4, "Chemical Specialties").

- Nonsettling solids (see Section 2.2.4.3).

Pollution prevention approaches for these materials are reviewed in other sections, as indicated. They originate from a wide variety of sources in wet processing. Color originates from print paste dumps, color kitchens, screen and squeegee cleaning, dye bath, and continuous dyeing mix discharges. Metals generally have the same sources as color, plus print screen making, photograph laboratory processes, and contamination from high-volume raw materials (e.g., salt, size). Solvents derive from nonaqueous printing thickeners, machine cleaning, screen cleaning, and shop uses. Nonsettling solids come from coating, dyeing, finishing, print pastes based on acrylic materials, warp size materials (e.g., gums and synthetic sizes), and foam from coating or carpet printing (45).

#### 2.2.5 Metals

The presence of metals in textile mill effluents is of concern primarily because of their toxicity to aquatic and mammalian species (8, 11,21). Metals also inhibit waste treatment operations and are difficult to remove or treat using pollution control technologies (11, 21).

##### 2.2.5.1 Sources

The sources of metals can be difficult to identify in textile operations; locating metals sources requires careful examination of all aspects of plant operations (21). Among the possible sources are: incoming fiber, water, dyes, plumbing, and chemical impurities. The presence of metals in effluent is a worldwide concern (44). All industries in Europe, including the textile industry, are required to reduce 36 specific substances, including heavy metals such as chromium, copper, nickel, and zinc by 50 percent or more. In addition, 70-percent reductions of mercury, cadmium, and lead are required (44). Many textile mills have little or no metals in their effluent but, whenever metals are present, they often include those shown in Table 2-16. The table indicates only harmful metals. Materials such as iron are not listed.

##### Dyes

Some dyes include metals that are known to be toxic such as copper (46). Metals can be present in dyes for two different reasons. First, mercury or other metals are used as catalysts during the manufacture of some dyes and can be present as a by-product (47). Second, some dyes include metals as an integral part of the dye molecule (47).

Dye manufacturers now are considering the environmental impact of the dyes that they produce, in addition to traditional concerns such as economy, higher wet fastness, and high tinctorial value. Many anthraquinone

**Table 2-16. Typical Sources of Metals in Effluent**

Metal	Typical Sources
Arsenic	Fibers, incoming water, fugitive, treated timber
Cadmium	Impurity in salt
Chrome	Dyes, laboratory
Cobalt	Dyes
Copper	Dyes, incoming water, fiber
Lead	Dyes, plumbing, shop
Manganese	Permanganate strip (repair mildew)
Mercury	Dye/commodity chemical impurity
Nickel	Dyes
Silver	Photo operations
Tin	Finishing chemicals, plumbing
Titanium	Fiber
Zinc	Dyes, impurity in commodity chemicals, incoming water, plumbing

dyes are derived by sulfonation in the presence of mercury catalysts. The mercury can cause pollution problems during the manufacture of the dye. Some dye manufacturers (in Japan, for example) use mercury-free manufacturing practices (48).

**Dyes Based on Metals.** For dyes that contain metals as an integral part of the dye molecule, the metallic content is essential to the dye's performance as a textile colorant. The metals most commonly found in dyes as part of the dye structure are shown in Table 2-17 (8).

In addition to the dyes listed in Table 2-17, other types of dyes can also contain metals, notably yellow pigments based on lead chromate and orange pigments based on molybdate (49). Also, some other pigments of various colors are based on cadmium (49). Other studies (14, 45) present lists of dyes and printing inks that contain metals. The metal content of dyes easily can be determined by consulting the MSDS for the dye or the CI (11).

**Table 2-17. Typical Metals Found in Dyes by Dye Class (8)**

Dye Class	Typical Metals in Structure <sup>a</sup>
Direct	Copper
Fiber Reactive	Copper and nickel
Vat	None
Disperse	None
Acid	Copper, chrome, cobalt
Premets	Copper, chrome, cobalt
Mordant	Chrome

<sup>a</sup> Does not imply that all dyes contain these metals.

The issue of "bound" versus "unbound" metal often is raised regarding the metal content of dyes. Bound metals are those in which the metal is chelated with the dye molecule, forming an integral structural element. More specifically, the empty d-orbitals of the metal ions are supplied with electrons donated from organic ligands such as ethylene diamine triacetic acid (EDTA), diethylene triamine penta acetic acid (DTPA), nitrilo triacetic acid (NTA), or various substituents in the dye molecule. An unbound metal is one that is not structurally bound to the dye molecule but that simply exists in some quantity in the dye formulation.

Dye companies often point out that bound metals exhibit lower toxicity than free metals and that bound metals tend to exhaust onto the substrate in dyeing so that they are not discharged with the wastewater. Not all dye in the dye bath, however, is exhausted (see Sections 2.2.1, "Color Residues in Dyeing Wastewater," and 4.3, "Dyes"). Furthermore, not all dye wastes come from the dyebath; dye wastes also result from handling, weighing, small-scale routine working losses, implement and drum cleaning, and spills. Important factors to consider are that EDTA, DTPA, NTA, and dye molecules are susceptible to biological degradation and that secondary activated-sludge aerobic treatment of the metal/ligand chelate produces free metals (50, 51). As the chelate degrades in the waste treatment system, metals are released as either precipitate in the sludges or in pass-through that is discharged in wastewater (50,51). Also, at this time EPA regulations do not recognize any distinction between bound and unbound metals.

**Dyes With Low-Level Metal Impurities.** ADMI analyzed 1,298 dyes by x-ray fluorescence that do not contain bound metal as an integral part of the dye molecule for eight metals (arsenic, cadmium, chromium, cobalt, copper, lead, mercury and zinc), as shown in Table 2-18. Specific dyes within the various classes can contain significant amounts of metals. The data do not include dyes that are known to be metal-bearing as bound, integral parts of the dye structure. The metals numbers in Table 2-18 are based on casual metal in dyes (47). Table 2-19 lists specific dyes having relatively high copper content (45). Note that these data are somewhat dated but represent the only detailed analysis of the metal content of dyes.

### **Dyeing Processes**

Other sources of metals include the dyeing process. Several sources in dyeing are not directly related to the dyestuffs themselves, including afterchrome processes for wool and clearing or discharge printing; copper after-treatments for certain direct dyes, and impurities in fibers, salt, caustic, and soda ash; as well as chemical oxidizers and reducers.

Afterchrome processes for wool dyeing are discussed below and also are discussed in Section 4.3, "Dyes," and 4.10, "Dyeing." Some mills may still use afterclearing or

**Table 2-18. Average Metal Concentration of Selected Dyes (47)**

Metal	Number of Dyes Tested and Average Metal Concentration by Dye Type <sup>a</sup>					
	Acid	Basic	Direct	Disperse	Fiber Reactive	Vat
Arsenic	413	137	313	177	46	58
	<1	<1	<1	<1	1.4	<1
Cadmium	417	137	313	177	46	58
	<1	<1	<1	<1	<1	<1
Chromium	404	137	303	117	46	58
	9	2.5	3	3	24	83
Cobalt	300	135	271	154	46	58
	3.2	<1	<1	<1	<1	<1
Copper	399	136	285	153	46	59
	79	33	35	45	71	110
Lead	408	135	315	161	46	58
	37	6	23	37	52	6
Mercury	450	132	350	196	46	94
	<1	0.5	0.5	<1	0.5	1
Zinc	421	122	311	166	46	59
	<13	32	8	3	4	4

<sup>a</sup> Top figure in each cell indicates the number of dyes tested; bottom figure indicates average metal concentration.

**Table 2-19. Dyes With High Copper Content (45)**

Dye	Copper Content (%)
Belamine F Red 3BL	4.00
Belamine B Blue LT	3.68
Pyrazol F Violet MXD	3.00
Solantine Brown BRL	3.00
Atlantic Blue 8GLN-K	2.70
Atlantic Resinifast Blue 2R	2.50
Sirius Supra Turquoise LG	2.29
Superlitefast Blue 2GLL	1.00
Direct Navy OFS	0.70
Belamine Red 3BL	4.00
Solophenyl Brown BRL	3.00
Fastolite Blue L	2.70
Atlantic Black NR	1.50

from dyeing processes. Fibers contain many types of metals at low levels (52). Copper sulfate was discontinued as an aftertreatment for direct dyes such as CI Direct Blue 98 at least 30 years ago, although some authors still write about this topic.

*Afterchrome Dyeing.* A study group of the International Wool Secretariat (IWS) identified four high-priority areas, including the reduction of chromium in wool processing wastewater from chrome dyeing (53). Approximately 70 percent of wool dyeing currently uses heavy metals, primarily chrome. Development of low-chrome methods has been underway since 1976. Results of these methods show reductions from approximately 155 ppm for conventional dyeing to levels of about 33 ppm, 8 ppm, and near 0 ppm for pH control, fresh bath, and thiosulfate methods, respectively. The best solution would be to develop black and navy dyes that do not require chrome (53). These, however, are not currently available.

discharge printing with zinc-stabilized reducing agents (for disperse dyes on polyester). The technical literature refers to these agents as "zinc sulfoxylate formaldehyde." These agents are discussed under oxidizing and reducing agents below. Chemical oxidizers containing manganese and chrome also are used in dyeing. In the 1960s, the use of dichromate was phased out (see discussion of oxidizers below). Impurities (e.g., zinc, mercury) in salt, caustic, and soda ash also can come

Another development is azo dyes based on iron instead of other more harmful metal ions such as cobalt, nickel, chromium, nickel, lead, and zinc. Research already has shown promise in substituting iron for cobalt in Acid Red 182 and Acid Blue 171 and substituting iron for chromium in Acid Black 172. These new dyes are nonmutagenic and do not introduce metals into dyeing wastewater (4). Commercialization of these dyes is still several years away, however.

## Plumbing

Metals can derive from plumbing, pumps, valves, and other similar sources. Combining galvanized pipes with brass fittings, valves, pump impellers, or other parts is a common mistake, leading to galvanic reactions when the pipes are exposed to acids, alkalis, or very high salt concentrations found in textile processing solutions and wastewater. These reactions liberate zinc from the galvanized surface.

Metals in a mill's influent raw water supply (notably copper in city water) can exchange ions with solder joints in plumbing, producing lead or tin effluent wastewater.

Residues can collect in wood, asphalt, soil, or old, cracked or porous concrete sumps, pits, trenches, drains, and treatment systems. These sorbed metals can be released slowly over a period of months or even years. This fugitive source of metals often defies easy identification.

## Chemicals

Sources of metals may also include chemicals used in textile processing, as described in the following paragraphs.

**Oxidizing and Reducing Agents.** During the 1940s and 1950s, the use of dichromate and permanganate as oxidizers was common in textile mills, contributing to high chromium levels in effluent. Zinc sulfoxylate formaldehyde reducing agents also were common. Zinc sulfoxylate formaldehyde is used for afterclearing and for discharge printing and stripping (i.e., repair work) (54). During the last 30 years, however, most mills have replaced these chemicals with the substitutions shown in Table 2-20.

**Finishes Containing Metals.** Certain textile finishes contain metals, including:

- *Antifungal and odor-preventive finishes:* Used for socks and based on organo-tin compounds.

**Table 2-20. Replacements for Dichromate, Permanganate, and Zinc Oxidizing Agents**

Previous	Replaced With
Dichromate	Peroxide Periodate Perborate Air
Permanganate	None, but the main necessity for permanganate was mildew removal repair procedure, and mildew control has improved with the advent of air-conditioned warehouses. In other words, the need has been eliminated.
Zinc-reducing agents	Sodium hydrosulfite ("hydro")

- *Water repellents:* Based on chrome chloride stearic acid adducts (55).
- *Flame retardants:* Based on either decabromobiphenyl oxide plus antimony oxide or titanium chloride for wool (55).

From a pollution prevention point of view, controlling releases of these metals in finishes is a matter of ensuring appropriate handling practices, worker training, control of pad dumps and mix discards, auditing, and other processes (14, 21).

**Low-Level Metal Impurities in Commodities.** Fibers received in wet processing operations can contain significant amounts of metals. Table 2-21 shows concentrations of calcium, magnesium, iron, copper, manganese, and zinc brought to the bleaching stage in raw cotton (52). These concentrations exceed the raw water supply concentrations because of the leaching of metals from the cloth being processed. Table 2-22 shows the results of testing two cotton samples for trace elements (including metals). Natural fibers can absorb metals from the environment. For example, raw cotton has been found to contain metals at levels between 75 and 100 ppm, which could translate to up to 10 ppm in wet processing effluent. Sources of metals include agricultural residues for natural fibers (e.g., arsenic), polymerization catalysts and delusterants in synthetic fibers (e.g., copper, titanium), and impurities added to fibers (e.g., in warp size) (21). Low-level metals are a significant problem. Salt, caustic, soda ash, and other chemicals also contain trace amounts of zinc, cadmium, and mercury.

Although the impurities in fibers and commodity chemicals are present in ppm or smaller quantities, a large operation can use, in the aggregate, several million pounds per week of commodity raw materials. The net

**Table 2-21. Contaminants in Processing Solutions in Textile Mills: Peroxide Saturator Solutions From Three Mills Bleaching Cotton Fabric in J Boxes' (52)**

Metal	Dissolved Metal in Processing Solution (ppm) <sup>b</sup>		
	Average of 14 Samples <sup>c</sup>	Range	
		Lowest	Highest
Calcium	68	28	130
Magnesium	24	7.7	49
Iron	1.5	0.5	3
Copper	0.25	0.065	0.68
Manganese	0.03	0.01	0.06
Zinc	0.49	0.14	0.8

<sup>a</sup> H<sub>2</sub>O<sub>2</sub>; 35% 15 to 30 g/L; sodium silicate, 42 Be., 15 to 39 g/L.

<sup>b</sup> As metal. Tests performed by Industrial Testing Laboratories, Inc., 2350 Seventh Boulevard, St. Louis, MO 63104.

<sup>c</sup> From four trials each in two mills and six trials in one mill.

**Table 2-22. Trace Element Analysis of Cotton After Preparation (51)<sup>a</sup>**

Element	Sample I (ppm)	Sample II (ppm)
Titanium	2.11 ± 5%	<0.5
Iodine	0.140 ± 7%	0.0104 ± 7%
Manganese	1.632 ± 0.5%	1.741 ± 0.5%
Magnesium	7.24 ± 15%	9.80 ± 15%
Copper	2.29 ± 8%	3.16 ± 8%
Vanadium	0.070 ± 10%	0.032 ± 10%
Chlorine	24.156 ± 5%	21.32 ± 5%
Aluminium	33.91 ± 1%	29.45 ± 1%
Mercury	<0.010	<0.010
Samarium	<0.005	<0.005
Uranium	<0.001	<0.001
Lanthanum	<0.4	<0.4
Cadmium	<0.8	<0.8
Gold	<0.0001	<0.0001
Arsenic	<0.2	<0.2
Antimony	<0.05	<0.06
Bromine	1.081 ± 1%	0.131 ± 5%
Sodium	<500.0	<500.0
Potassium	<500.0	<500.0
Cerium	<0.2	<0.2
Calcium	<100.0	<100.0
Selenium	<0.1	<0.1
Thorium	<0.004	<0.004
Chromium	0.095 ± 7%	0.142 ± 3%
Europium	<0.001	<0.001
Ytterbium	<0.03	<0.03
Barium	<5.0	<5.0
Cesium	0.0076 ± 10%	0.0083 ± 10%
Silver	<0.005	<0.005
Nickel	<5.0	<5.0
Scandium	0.0038 ± 2%	0.0038 ± 2%
Rubidium	<20.0	<30.0
Iron	68.29 ± 10%	60.04 ± 10%
Zinc	7.38	7.35
Cobalt	0.017	0.024
Molybdenum	<1.0	<1.0

<sup>a</sup> Neutron activation analysis of trace elements in cotton fabric.

effect is to generate significant amounts of metals in wastewater.

**Raw Water.** Metals often are found in incoming water, as city drinking water supplies can often contain more than 1 ppm of zinc, copper, and/or iron (21). Tests

reported in Smith (4) in the southeastern United States, however, showed levels below 0.1 ppm for each of these (see Table 2-23). Copper is added to public water systems to control algae growth in tanks and ponds. Aluminum, in the form of alum, is another commonly added material. These metals can undergo ion exchange with plumbing (especially lead solder joints), valves, and pump parts to produce lead or other less electromagnetic metals in the mill's effluent.

### 2.2.5.2 Pollution Prevention Strategies

Procedures to reduce or eliminate metals must start with identification of metals and their sources and follow with an analysis of metals levels to determine the relative importance of that metal pollution. Identification can be made either by analysis of effluent or examination of input chemicals and process requirements, such as water. General pollution prevention methods of reducing or eliminating metals include:

- Careful prescreening of all chemicals (see Section 3.12, "Raw Material Prescreening Before Use").
- Substituting for metal-containing compounds (e.g., with nonmetal dyes).
- Improving efficiency of the process or operations by lowering chemical use while maintaining product quality objectives, perhaps by means of automation. Another method is to improve management of operations (e.g., better chemical handling skills).
- Elimination of galvanized plumbing.

**Table 2-23. Raw Water Quality in Textile Mills in Southeastern United States (52)<sup>a</sup>**

Constituent	Equivalency	Concentration of Constituents (ppm)		
		Average of 10	Lowest	Highest
Calcium	CaCO <sub>3</sub>	12.9	1	46.5
Magnesium	CaCO <sub>3</sub>	3.8	1.5	7.8
Sodium	CaCO <sub>3</sub>	36	5.7	76.1
Alkalinity				
Bicarbonate	CaCO <sub>3</sub>	27.7	10	110
Carbonate	CaCO <sub>3</sub>	1.4	0	10
pH	—	7.2	5.7	7.8
Iron	Fe <sup>2+</sup>	0.1	0.01	0.31
Copper	Cu <sup>2+</sup>	0.02	0.01	0.1
Manganese	Mn <sup>2+</sup>	0.01	0	0.05
Zinc	Zn <sup>2+</sup>	0.11	0	0.24

<sup>a</sup> Tests performed by Industrial Testing Laboratories, Inc., 2350 Seventh Boulevard, St. Louis, MO 63104.

As metals analysis has improved over the years and detection limits have decreased, regulatory limits on metals have also been lowered. Regulatory authorities may now set metals limits for some mills in the low ppb range. For example, a small textile operation discharging 50,000 gallons of wastewater per day with a 3-ppb limit on a particular metal discharges less than 200 milligrams of metal per day.

Dyes without metals should be used wherever possible. If a shade cannot be matched with a metal-free color (as is often the case with bright green and royal blue direct and fiber reactive colors), reducing the metal-bearing dye content is often possible by substituting part of the dye. In the case of green shades, brighter blues and greens contain metals. In the example shown below, a blue/yellow/red match of a green shade could be substituted with a lower metal version by replacing the red with a duller, but non-metal-bearing blue. This substitution could carry the necessary dullness in the shade and at the same time reduce the amount of metal-bearing brilliant blue in the recipe:

**Best Match Recipe**

1.4 percent	Metal-bearing blue
2.0 percent	Yellow
0.1 percent	Red for shading

**Alternative Reduced-Metal Match**

0.5 percent	Metal-bearing blue
0.8 percent	Non-metal-bearing blue
1.7 percent	Yellow
No red shading color because nonmetallic blue is duller	

As a good pollution prevention practice, a mill should always insist on knowing the CI designation of all dyes used, in addition to their pollution status, including metal content. This issue is important because some of the major dye companies have withdrawn support for the CI system.

Pollution prevention strategies for dealing with metal-containing dyes are to:

- Seek substitutes (for all or part of the metal-containing dye) that do not contain metal (14, 45). Table 2-24 provides a good selection of fiber reactive dyes that do not contain metal as a component of the dye structure (8).
- Ensure maximum fixation by optimizing the process (45).
- Provide special auditing, handling, and worker training where these dyes are used. Special handling and use procedures for metal-bearing materials (e.g., segregating waste streams with separate plumbing

**Table 2-24. Non-Copper-Containing Direct and Fiber Reactive Dyes**

Yellow 50	Red 153
Yellow 106	Blue 75
Orange 37	Blue 98
Red 76	Blue 106
Red 80	

systems) are necessary in some cases to keep metals out of the wastewater and to reduce aquatic toxicity (21).

Using disperse dyes that can be aftercleared with caustic (alkali) only eliminates the need for reducing agents (e.g., hydro), which can contribute BOD and, in some cases, metals to the effluent (48).

**2.2.6 Aquatic Toxicity**

Compounds that contribute to aquatic toxicity are a particular environmental concern for all industry. The national policy prohibiting discharge of toxic pollutants is embodied in Section 101 (a)(3) of the federal Clean Water Act. EPA has identified toxic compounds under the general heading "Priority Pollutants," numbering approximately 126 compounds in 65 classes (see Table 2-25). Categorical discharge standards regulate these compounds. EPA identified priority pollutants on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity (56).

**2.2.6.1 Aquatic Toxicity of Textile Wastewater**

The aquatic toxicity of textile industry wastewater varies considerably among production facilities. Data are available that show that some facilities have fairly high aquatic toxicity, while others show little or no toxicity. Table 2-26 summarizes the results for about 75 mills in North Carolina.<sup>5</sup> Of the mills tested, effluent from about one-half showed no toxicity. The median value of all positive tests was 48.5 percent, indicating that a 48.5 percent solution of the mill's treated effluent caused 50-percent mortality among tested organisms.

**2.2.6.2 Testing for and Determining Toxicity**

Numerous compounds in textile effluent can contribute to aquatic toxicity, including dyes, dyeing auxiliaries, and surfactants. Identifying all the toxic compounds used in textile production is impossible because of the huge variety of chemicals used and the lack of data on their toxicities. Several methods may be used, however, to identify compounds of concern. Knowledge of the chemical compounds used by a mill and their associated toxicities (or classes of toxicity) can help

<sup>5</sup> Tedder, S.W. 1986. Aquatic bioassay toxicological summary (memorandum). North Carolina Division of Environmental Management, Raleigh, NC (March 31).

Table 2-25. List of EPA Priority Pollutants<sup>a</sup>

Code	CAS <sup>b</sup> No.	Pollutant
P058	100027	4-nitrophenol
P038	100414	Ethylbenzene
P101	1024573	Heptachlor epoxide
P034	105679	2,4-Dimethylphenol
P027	106467	1,4-Dichlorobenzene
P002	107028	Acrolein
P010	107062	1,2-Dichloroethane
P003	107131	Acrylonitrile
P042	108602	Bis(2-chloroisopropyl) ether
P086	108883	Toluene
P007	108907	Chlorobenzene
P065	108952	Phenol
P019	110758	2-chloroethyl vinyl ether (mixed)
P111	11096825	PCB-1260 (aroclor 1260)
P107	11097691	PCB-1254 (aroclor 1254)
P108	11104282	PCB-1221 (aroclor 1221)
P109	11141165	PCB-1232 (aroclor 1232)
P018	111444	Bis(2-chloroethyl)ether
P066	117817	Bis(2-ethylhexyl)phthalate
P009	118741	Hexachlorobenzene
P078	120127	Anthracene
P008	120821	1,2,4-Trichlorobenzene
P031	120832	2,4-Dichlorophenol
P035	121142	2,4-Dinitrotoluene
P037	122667	1,2-Diphenylhydrazine
P051	124481	Chlorodibromomethane
P110	12672296	PCB-1248 (aroclor 1248)
P085	127184	Tetrachloroethylene
P084	129000	Pyrene
P071	131113	Dimethyl phthalate
P116	1332214	Asbestos (fibrous)
P129	1746016	2,3,7,8-Tetrachlorodibenzo-P-dioxin (TCDD)
P079	191242	1,1,2-Benzoperylene (benzo(ghi)perylene)
P083	193395	Indeno(1,2,3-cd)pyrene (2,3-o-phenylenepyrene)
P074	205992	3,4-Benzofluoranthene (benzo(b)fluoranthene)
P039	206440	Fluoranthene
P076	218019	Chrysene
P089	309002	Aldrin
P102	319846	Alpha-BHC
P103	319857	Beta-BHC
P105	319868	Delta-BHC
P093	3547044	4,4'-DDE (p-p'-DDX)
P092	50293	4,4'-DDT
P073	50328	Benzo(a)pyrene (3,4-Benzopyrene)
P059	51285	2,4-Dinitrophenol
P060	534521	4,6-Dinitro-o-cresol
P106	53469219	PCB-1242 (aroclor 1242)
P082	53703	1,2,5,6-Dibenzanthracene (dibenzo(a,h)anthracene)
P033	542756	1,3-Dichloropropylene (1,3-Dichloropropene)

Table 2-25. List of EPA Priority Pollutants<sup>a</sup> (Continued)

Code	CAS <sup>b</sup> No.	Pollutant
P017	542881	Bis(chloromethyl)ether (deleted)
P006	56235	Carbon tetrachloride (tetrachloromethane)
P072	56553	1,2-Benzanthracene (benzo(o)anthracene)
P121	57125	Cyanide (total)
P091	57749	Chlordane (technical mixtures and metabolites)
P104	58899	Gamma-BHC (lindane)
P022	59507	Parachlorometacresol
P090	60571	Dieldrin
P036	606202	2,6-Dinitrotoluene
P063	621647	N-nitrosodi-n-propylamine
P061	62759	N-nitrosodimethylamine
P023	67663	Chloroform (trichloromethane)
P012	67721	Hexachloroethane
P004	71432	Benzene
P011	71556	1,1,1-Trichloroethane
P098	72208	Endrin
P094	72548	4,4'-DDD (p,p'-TDE)
P122	7439921	Lead (total)
P123	7439976	Mercury (total)
P124	7440020	Nickel (total)
P126	7440224	Silver (total)
P127	7440280	Thallium (total)
P114	7440360	Antimony (total)
P115	7440382	Arsenic (total)
P117	7440417	Beryllium (total)
P118	7440439	Cadmium (total)
P119	7440473	Chromium (total)
P120	7440508	Copper (total)
P128	7440666	Zinc (total)
P046	74839	Methyl bromide (bromomethane)
P045	74873	Methyl chloride (chloromethane)
P016	75003	Chloroethane
P088	75014	Vinyl chloride (chloroethylene)
P044	75092	Methylene chloride (dichloromethane)
P047	75252	Bromoform (tribromomethane)
P048	75274	Dichlorobromomethane
P013	75343	1,1-Dichloroethane
P029	75354	1,1-Dichloroethylene
P050	75434	Dichlorofluoromethane (deleted)
P049	75694	Trichlorofluoromethane (deleted)
P100	76448	Heptachlor
P053	77474	Hexachlorocyclopentadiene
P125	7782492	Selenium (total)
P054	78591	Isophorone
P032	78875	1,2-Dichloropropane
P014	79005	1,1,2-Trichloroethane
P087	79016	Trichloroethylene
P015	79345	1,1,2,2-Tetrachloroethane
P113	8001352	Toxaphene
P070	84662	Diethyl phthalate
P068	84742	Di-n-butyl phthalate

**Table 2-25. List of EPA Priority Pollutants<sup>a</sup> (Continued)**

Code	CAS <sup>b</sup> No.	Pollutant
P081	85018	Phenanthrene
P067	85687	Butyl benzyl phthalate
P062	86306	N-nitrosodiphenylamine
P080	86737	Fluorene
P052	87683	Hexachlorobutadiene
P064	87865	Pentachlorophenol
P021	88062	2,4,6-Trichlorophenol
P057	88755	2-nitrophenol
P055	91203	Naphthalene
P020	91587	2-chloronaphthalene
P028	91941	3,3-Dichlorobenzidine
P005	92875	Benzidine
P025	95501	1,2-Dichlorobenzene
P024	95578	2-chlorophenol
P056	98953	Nitrobenzene
P030	NA <sup>c</sup>	1,2-Trans-dichloroethylene
P069	NA	Di-n-octyl phthalate
P096	NA	Beta-endosulfan
P097	NA	Endosulfan sulfate
P112	NA	PCB-1016 (aroclor 1016)
P026	NA	1,3-Dichlorobenzene
P095	NA	Alpha-endosulfan
P001	NA	Acenaphthene
P041	NA	4-bromophenyl phenyl ether
P075	NA	1,2-Benzofluoranthene (benzo(b)fluoranthene)
P040	NA	4-chlorophenyl phenyl ether
P043	NA	Bis(2-chloroethoxy) methane
P077	NA	Acenaphthylene
P099	NA	Endrin aldehyde

<sup>a</sup> 46 CFR 2264 (January 1981).

<sup>b</sup> CAS = Chemical Abstract Service.

<sup>c</sup> NA = not applicable.

predict whether an effluent toxicity problem exists. One source of information is MSDSs, which list chemical ingredients, their known toxic effects, and other characteristics. Other sources include manufacturer formulations if they are listed or can be provided by the manufacturer. Analysis of these compounds or of the effluent to determine their precise chemical nature (including toxicity) is, practically speaking, impossible.

Another approach for assessing toxicity is to measure whole effluent toxicity (chronic or acute), without regard to the specific chemical compound(s) that contributes to toxicity. The textile industry produces many thousands of compounds in effluent, and identifying and testing all of them is impractical. As a result, toxicity testing of the whole effluent stream on aquatic organisms is a cost-effective means of determining overall toxicity. Toxicity testing proceeds by exposing freshwater, estuarine, and marine life forms in tanks to either stationary, renewed, or flowing effluent. Species tested include algae, shrimp, silversides, and minnows. Toxicity is calculated in vari-

**Table 2-26. Results From Aquatic Toxicity Testing of Effluent From 75 Textile Mills<sup>a,b</sup>**

Toxicity (%)	Number of Tests in That Range
<9	7
10-19	6
20-29	8
30-39	2
40-49	4
50-59	9
60-69	3
70-79	8
80-89	2
90-100	3
>100 (no toxicity)	38

<sup>a</sup> Toxicity in the table is LC<sub>50</sub> in percent; thus, higher numbers represent lower toxicity.

<sup>b</sup> See footnote 2.

ous ways: measuring death rates, observing birth defects, and noting other biological indications. One common measure of toxicity is LD<sub>50</sub>, which stands for lethal dose 50 percent, meaning the amount of chemical dose required to cause mortality in 50 percent of the test population. LC<sub>50</sub> (lethal concentration 50 percent), another common measure, represents the concentration of effluent in the dilution water that causes mortality in 50 percent of the test population (56).

### 2.2.6.3 Types of Toxic Chemical Compounds

The sources of aquatic toxicity in textile wastewater can be hard to identify (21). Despite the lack of knowledge concerning the exact composition or toxicity of many textile dyes and auxiliary chemicals, many generally known groups of chemical agents contribute to aquatic toxicity of textile wastewater. These agents include (21):

- Salt
- Surfactants
- Metals
- Toxic organic chemicals
- Biocides
- Toxic anions

Examples of compounds in each of these classes and their sources are shown in Table 2-27. Information related to the toxicity of these compounds and pollution prevention strategies effective for each are discussed in the following paragraphs. In addition, each category is also discussed in other chapters of this document. These sections provide further details concerning

**Table 2-27. Typical Causes of Aquatic Toxicity**

Agent	Chemical Example	Typical Source
Salt	NaCl, Na <sub>2</sub> SO <sub>4</sub>	Dyeing
Surfactants	Ethoxylated phenols	Multiple sources
Metals	Copper, zinc, etc.	Dyes
Organics	Chlorinated solvents	Scour, machine cleaning
Biocides	Pentachlorophenol	Wool fiber contaminant
Toxic anions	Sulfide	Sulfur dyeing

amounts, sources, and appropriate pollution prevention practices.

**Dyes**

Most textile dyes have low aquatic toxicity. A study of 46 commercially important dyes, summarized in Table 2-28, showed that 29 (60 percent) had very low aquatic toxicity of (LC<sub>50</sub> greater than 180 ppm) (57). The toxicity distribution of the dyes is shown in Table 2-29.<sup>6</sup> The numbers indicate that, for example, 7 of the 46 dyes exhibited toxicity at concentrations of between 1 and 10 ppm.

For the few dyes that exhibit higher toxicity characteristics, it is important to realize the degree of dilution that normally occurs.

- A typical batch (exhaust) dyebath using 1 percent dye owg at 10:1 bath ratio contains 1,000 ppm of dye.
- If the dye is 90 percent exhausted onto the fabric, the concentration would drop to 100 ppm in the spent dyebath.
- When combined with other process wastewater from processes such as preparation, or washing off, the concentration drops to about 5 ppm. (Note: assumes millwide water consumption of 20 gallons per pound of fabric at 8.34 pounds per gallon.)
- Assuming that the in-stream concentration/dilution factor for the textile wastewater is 10 percent in the receiving stream (a fairly severe assumption), the “in-stream concentration” would be less than 1 ppm. This assumes that none of the color is removed in treatment and that the toxicity of the degradation products is equal to that of the original dye.

If the spent dyebath is combined, however, with cleanup waste, spilled dye, and discarded mixes, the in-stream value could be higher.

As a class, certain types of dyes exhibit higher toxicity than others. Table 2-30 shows the toxicity of the 47 dyes

<sup>6</sup> Note that this study used purified dyes. Typical commercial dyes contain 20 to 80 percent other materials; thus, toxicities of in-use dyes should be 20 to 80 percent below those reported for the pure substances.

**Table 2-28. Effect of 46 Selected Dyes on the Fathead Minnow, *Pimephales Promelas*, in Static Bioassay Tests (57)**

C.I. Number	Dye	LC <sub>50</sub> , 96 Hour (mg/L)	Temperature (°C)
10338	Disperse Yellow 42	>180	15
11855	Disperse Yellow 3	>180	15
14645	Mordant Black 11	6	15
15510	Acid Orange 7	165	17
15711	Acid Black 52	7	15
18965	Acid Yellow 17	>180	17
19555	Direct Yellow 28	>180	15
20170	Acid Orange 24	130	17
20470	Acid Black 1	>180	15
21010	Basic Brown 4	5.6	20
22610	Direct Blue 6	>180	17
24401	Direct Blue 218	>180	17
24890	Direct Yellow 4	>180	15
24895	Direct Yellow 12	125	15
25135	Acid Yellow 38	23	15
26360	Acid Blue 113	4	15
28160	Direct Red 81	>180	17
29025	Direct Yellow 50	>180	17
29160	Direct Red 23	>180	17
20145 (or 30145)	Direct Brown 95	>180	17
30235	Direct Black 38	>180	17
31600	Direct Black 80	>180	17
40000	Direct Yellow 11	>180	17
40622	Fluorescent Brightening Agent 28	>180	17
42000	Basic Green 4	0.12	18
42535	Basic Violet 1	0.047	15
47020	Disperse Yellow 54	>180	15
48055	Basic Yellow 11	3.2	18
51005	Basic Blue 3	4	15
53185	Sulfur Black 1	>180	15
53630	Vat Blue 43	>180	15
59105	Vat Orange 1	>180	15
59825	Vat Green 1	>180	15
61505	Disperse Blue 3	1	15
61570	Acid Green 25	6.2	18
62055	Acid Blue 25	12	15
62500	Disperse Blue 7	52	15
63010	Acid Blue 45	>180	15
67300	Vat Yellow 2	>180	15
69015	Vat Brown 3	>180	15
69500	Vat Green 3	>180	15
69825	Vat Blue 6	>180	15
74180	Direct Blue 86	>180	17
NA <sup>a</sup>	Acid Yellow 151	29	15
NA	Disperse Red 60	>180	15
NA	Direct Yellow 106	>180	17

<sup>a</sup> NA = not available.

**Table 2-29. Frequency Distribution of Toxicity Test Results for 46 Commercial Dyes (57)**

Toxicity Range (LC <sub>50</sub> ppm)	Number of Dyes in Range	Percent of Total
>180	29	63.0
100-180	3	6.5
10-100	4	8.7
1-10	7	15.2
0.1-1	2	4.3
<0.1	1	2.2
Totals	46	100.0

by dye class. Cationic materials generally are very toxic. Fortunately, cationic dyes exhaust essentially 100 percent in batch dyeing operations (see also Section 4.3, "Dyes"). At the time of this study, the fiber reactive dyes that are now popular were not in widespread use. These would exhibit similar toxicity to acid and direct dyes except that they are typically accompanied in wastewater by large amounts of salt.

From the above, pollution prevention strategies can be directly deduced, including:

- Selecting nontoxic dyes if information is available.
- Using minimum amounts of dye.
- Using dyes of high tinctorial value.
- Ensuring maximum exhaustion of the dyebath by proper dyeing process, pH, salt, etc. (see Sections 2.2.1, "Color Residues in Dyeing Wastewater," and 4.3, "Dyes").
- Selecting treatable dyes that degrade to nontoxic products. Unfortunately, data on these dyes are not readily available to dyers.
- Maintaining proper processes such as special handling, worker training, recordkeeping for dyes of high toxicity (e.g., basic dyes).

### Surfactants

Surfactants and related compounds (detergents, emulsifiers, dispersants) are used in almost every textile process and can be an important contributor to effluent toxicity (and BOD). The wide variety of available alternatives allows for selection of less-polluting chemicals.

Quaternary amines used for processes such as disinfecting, scouring, softening are particularly toxic and should be avoided wherever possible (21). These are reviewed in detail in Section 4.4, "Chemical Specialties."

Surfactants are important in a large number of textile processes, including:

- Lubricating

**Table 2-30. Toxicities of Various Dye Classes (57)**

Dye Class	Number Tested	Number Toxic	Percent Found To Be Toxic
Disperse	6	2	33.3
Acid	12	8	66.7
Mordant <sup>a</sup>	1	1	100.0
Direct	14	1	7.1
Basic	5	5	100.0
Brightener	1	0	0.0
Sulfur	1	0	0.0
Vat	7	0	0.0
Fiber reactive	0	0	—

<sup>a</sup> Mordant is an obsolete class similar to acid dyes.

- Spin finishing
- Desizing
- Scouring
- Mercerizing
- Bleaching
- Wet finishing
- Foam finishing
- Dyeing
- Foam dyeing

Most textile surfactants are either nonionic or anionic. Nonionic surfactants dissolve in water without forming ions, while anionic surfactants form negative ions when dissolved in water. The major classes of each are:

- Nonionic surfactants:
  - Alcohol ethoxylates
  - Alkylphenol ethoxylates
- Anionic surfactants:
  - Alkylbenzene sulfonates
  - Alcohol ethoxysulfates

Surfactants are a major contributor to the aquatic toxicity of textile effluent and foaming. Nonionic surfactants of the type used in textile processing can be acutely toxic to aquatic life at levels as low as 1 ppm and can produce chronic effects in the 0.1 to 1.0 ppm range (58). Surfactants in raw textile waste have been found in concentrations ranging from 50 to 200 ppm (58). The concentration in treated effluent depends on the degree of biodegradation of the surfactant in the treatment plant. The choice of surfactant determines the degree of degradation and the ultimate concentration in discharged effluent. Linear alcohol ethoxylate (LAEs), linear alkylbenzene sulfonates, and alcohol ethoxysulfates are more biodegradable than APs (58-60) and thereby produce less foaming

in receiving waters. These are discussed in detail in Section 4.4, "Chemical Specialties."

*Salt.* Salts of various types are used as raw materials or are produced as by-products of other textile wet processes (e.g., neutralization). Several authors have identified the large amounts of salt used in textile dyeing, particularly in conjunction with fiber reactive dyes, as a significant future problem area for the textile industry (8).

Typical cotton batch dyeing operations use quantities of salt that range from 20 percent to 80 percent owg, and the usual salt concentration in such wastewater is 2,000 to 3,000 ppm (11). Federal guidelines for in-stream salt concentrations have been established at 230 ppm (21). The treatment of mixed wastewater to reduce salt to levels that meet such limits is extremely difficult and expensive by any known method. Pollution prevention is the only reasonable alternative to solve the dilemma presented by this hard-to-treat, toxic, and high-volume waste. General methods of dealing with salt are discussed in Section 2.2.2, "Discharge of Electrolytes." In addition, two specific methods for reducing salt requirements (pad-batch dyeing and dyebath reuse) are reviewed in detail in Section 4.10, "Dyeing."

*Toxic Organic Chemicals.* Textile effluents may contain numerous types of toxic organic compounds, both volatile and nonvolatile. In the 1980s, the state of North Carolina studied toxic materials (excluding surfactants) in wastewater from five textile wet processing mills that had shown aquatic toxicity in the past (61).<sup>7</sup> Results from these tests, shown in Table 2-31, identified between 8 and 42 toxic organic compounds.

Most of the identified materials were hydrocarbons. Several chlorinated organic solvents were detected, including perchloroethylene, trichlorobenzene, methylene chloride, and chloroform. Many esters were also detected, primarily benzoates, phthalates, and esters of hexanedioic acid. Other compounds identified included acetone, cyclohexanone, cyclohexanol, and other alcohols, such as 2-ethyl hexanol, and acids, such as hexadecanoic acid.

Halogenated organics, particularly organochlorines, are produced as a by-product of wool shrinkproofing processes. These chemicals are of concern when they later appear in receiving water or drinking water supplies as AOX. The chlorine/Hercosett process of shrink proofing wool with chlorine generates 39 milligrams AOX per liter of liquid discharged (53). This is far higher than the proposed United Kingdom standard of 1 milligram per liter (53).

The aquatic toxicities of numerous organics found in textile wastewater in the five-mill study are shown in

**Table 2-31. Toxic Organics Detected in Wastewater From Five Textile Wet Processing Mills (61)**

Site	Number of Toxic Organic Chemicals Identified		
	Volatiles	Nonvolatiles	Total
1	34	8	42
2	12	2	14
3	0	11	11
4	4	4	8
5	4	5	9

Table 2-32 (61). Of the approximately 50 compounds identified, aquatic toxicity data were readily available for only 11. This points to a basic problem in preventing aquatic toxicity: the lack of data on aquatic toxicity of chemical compounds. Also, in many cases, the chemical constitution of specialty chemical processing assistants is unknown to the user. Methods of addressing this problem are described in Section 4.4, "Chemical Specialties."

*Biocides.* Biocides are used for two major purposes in textiles: 1) to prevent biological growth during textile processing, and 2) as a finish to impart biocidal properties to textile products.

Biocides for in-process textile use include:

- Weed killers used around bulk storage tanks and buildings.
- Disinfectants for restrooms.
- Algae suppressants in air-cooling tower systems.
- Mildew inhibitors as a component of warp size.
- Biocides applied to sheep, a source of contaminants in wool.
- Defoliants and insecticides applied to cotton in farming.

**Table 2-32. Aquatic Toxicities of Organic Chemicals Found in Effluent From Five Textile Mills (61)**

Chemical	Aquatic Toxicity Range (ppm)
Acetone	>1,000
Chloroform	10-100 (animal carcinogen)
Cyclohexane	10-100
Cyclopentane	>1,000
Decahydronaphthalene	100-1,000
Ethyl benzene	10-100
Methylene chloride	100-1,000
Perchloroethylene	10-100 (animal carcinogen)
Trichlorobenzene	0-10
Xylene	10-100

<sup>7</sup> See footnote 2.

These may end up in effluent, sanitary wastewater, or stormwater discharges (runoff) from the industrial facility.

Several biocidal finishes are also applied to textile materials, including:

- Insecticides for carpets
- Mothproofing agents for wool
- Odor suppressants for socks/hosiery

The simplest, cheapest method of applying these compounds to wool products is through dyebath addition. Unfortunately, the biocides, such as permethrin, do not exhaust fully onto the fabric and consequently are discharged with the effluent.

Several European countries are now requiring textile operations to reduce discharges of specific pesticide materials, notably pentachlorophenol (PCP) for wool finishing and AOX (44). PCP and its salts and esters are used as industrial biocides to prevent deterioration of wood and cellulosic fibers. PCPs have been used in carpet manufacture, but their presence is not limited to wool carpets. Carpet backing materials, particularly jute, polypropylene, and latex, also contain PCP, often at levels greater than those found in wool fibers (62). PCP use on textile products has been criticized, and its use for indoor materials is banned in Germany, Sweden, Switzerland, Japan, and the United States (62).

In the United Kingdom, mothproofing of wool and wool blend carpets was previously performed using chlorophenylid-based agents; these have since been banned. Other mothproofing agents in use include permethrin and cyfluthrin. Permethrin is effective and has low toxicity to humans but high aquatic toxicity (63). Quantities of all three mothproofing agents are found in British rivers and current practices are not expected to comply with environmental quality standards (EQS) established in the United Kingdom (53). The discharge of leftover portions of processing baths is the main source of the problem (63). This is one of the four high-priority areas identified by the IWS study group (53).

Substitutes for permethrin and cyfluthrin are thus being sought. Diphenylurea and cyfluthrin can replace permethrin. Diphenylurea may exhibit less aquatic toxicity but, in some cases, is less biodegradable. A synthetic pyrethroid alternative to permethrin, cycloprothrin, exhibits good performance and has aquatic toxicity three orders of magnitude less than permethrin. Nippon Kayaku manufactures cycloprothrin and markets it as Cyclosal. The toxic properties are very low. The mammalian toxicity  $LD_{50}$  in rats and mice is greater than 5,000 milligrams per kilogram, and no irritant, carcinogenic, teratogenic, or mutagenic properties have been observed (64).

*Pesticide Residues.* Residues of pesticides used to prevent parasitic infestation on sheep may be present in effluent from wool scouring operations. At one time, many organochlorine pesticides were in widespread use, but many countries have banned these pesticides because of concerns over mammalian toxicity. Some countries still use organochlorine pesticides such as lindane (gamma-hexachlorocyclohexane), campheclor (or toxaphene), and dieldrin. Organophosphate and synthetic pyrethroids are more commonly used today. Both of these groups have lower mammalian toxicity and are less persistent in the environment than organochlorine pesticides, although they may still contribute to effluent toxicity.

The degradability of various chemical pesticides in wastewater treatment plants has been assessed in studies by Mickelson et al. (1). Dieldrin was degraded by 81 percent, dichlorofenthion by 79 percent, diazinon by 87 percent, cyperethrin-1 by 84 percent, cyperethrin-2 by 90 percent, and deltamethrin by 92 percent. These are discussed further in Section 4.12.4.

*Toxic Anions.* The main source of toxic anions in textile operations is sulfide from sulfur dyeing. Sulfides are very odiferous and toxic, and can be a significant problem in wastewater from sulfur dyeing.

When initially introduced in the late 1800s, sulfur dyes were reduced in the dyehouse by boiling the dye with soda ash and sodium sulfide to render them soluble (12). A by-product was foul-smelling sulfur dioxide. A later advance was the introduction in 1936 of prereduced/presolubilized sulfur dyes, which eliminated the need for onsite reduction processes. In the 1990s new types of sulfur dyes have been introduced that feature lower sulfide content, thus producing less sulfide in the effluent and fewer hydrogen sulfide odors in the mill and in the waste treatment system. The chemical nature of the proprietary reducer is not revealed, but it appears to be an organosulfur reducing agent (12).

One strategy for reducing sulfide in wastewater is to substitute glucose for sulfide-containing reducing agents (44). Even cheaper reducing sugars from corn can reportedly perform the same function. In one case, the sulfide concentration was reduced from 30 ppm to 2 ppm in the effluent. A small increase in BOD resulted, which was easily handled in the treatment system, whereas the sulfide waste was not amenable to waste treatment. The zone settling velocities of the clarifiers improved as a result of the decrease in sulfide, thus increasing waste treatment efficiency. In addition, odors decreased substantially.

The change to glucose did not increase operating costs. Estimated cost savings were \$20,000 per year from avoided costs for sulfide removal equipment, and a savings of \$30,000 per year in waste treatment opera-

tion costs. The corn sugars were a waste stream from the corn starch industry, and the corn starch manufacturer saved \$12,000 in waste treatment system expansion and \$2,400 in operating expenses (44).

**Other Toxic Compounds.** Other potential sources of toxicity in wastewater may be present in textile operations:

- Evidence shows that some dyes and other compounds have the potential to degrade from relatively safe forms into toxic compounds. For example, the dye FD&C Food Red #5, although not a textile dye, degrades into products that are both carcinogenic and mutagenic (46).
- Sequestering agents such as EDTA and DTPA form stable complexes with heavy metals. These complexes can pass right through a treatment plant and into receiving waters, where the compounds eventually break down, releasing the metals into the environment (50, 51).
- Phosphonates and polyphosphates can be used as dispersing agents as well as complexing agents. Both compounds have a low bioeliminability and have been banned in several countries because of eutrophication problems (50, 51).
- Four high-priority areas in wool finishing identified by the IWS study group are: 1) pesticide residues in wastewater from wool contaminated with pesticides, 2) discharge of mothproofing agents from wool carpet manufacture, 3) halo-organic compounds from wool shrinkproofing, and 4) chromium from chrome dyeing (53).

### ***Pollution Prevention Strategies***

Pollution prevention strategies for toxic chemical compounds include:

- Special handling and use procedures for the compounds described above may be necessary to keep them out of the wastewater. Strategies include employee training to improve awareness of the toxicity potential of priority compounds and improve their handling, separate plumbing to segregate these wastes and facilitate special treatment and screening procedures to identify ingredients and evaluate their potential contribution to toxicity before being put in use.
- Chlorinated solvents should be replaced with non-chlorinated types (21).
- Rapid, large pH variation can also produce aquatic toxicity and should be avoided (21).
- MSDSs are a good, but often limited, source of information. MSDS data focus on human exposure and toxicity, which may correlate with environmental effects. Some specific chemical types, however, may have low human toxicity but high aquatic toxicity

(e.g., quaternary amines). Other prescreening techniques are discussed in Section 3.12, "Raw Material Prescreening (Before Use)."

- Products, colors, and finishes that require the use of toxic production chemicals should be identified to the designer and to the consumer, and alternatives that can be produced more safely should be promoted. Many producers and consumers of textile products are aware of environmental concerns and factor information about environmental impacts into their purchasing decisions.
- Nonprocess chemicals, such as those used for cleaning, maintenance, and weed killing should receive special attention in terms of prescreening evaluation (see Section 3.12, "Raw Material Prescreening (Before Use)"), employee training (see Section 5.3, "Training Programs and Worker Attitudes"), as well as storage and handling in general (see Sections 3.8, "Maintenance, Cleaning, and Nonprocess Chemical Control," and 4.18, "Support Work Areas").
- Ultraviolet disinfection is a good replacement for biocides in cooling water towers.

### ***2.2.7 Water Conservation***

Water is used extensively throughout textile processing operations. Almost all dyes, specialty chemicals, and finishing chemicals are applied to textile substrates from water baths. In addition, most fabric preparation steps, including desizing, scouring, bleaching, and mercerizing, use aqueous systems.

The amount of water used varies widely in the industry, depending on the specific processes operated at the mill, the equipment used, and the prevailing management philosophy concerning water use. Reducing water consumption in textile processing is important for furthering pollution prevention efforts, in part because excess water use dilutes pollutants and adds to effluent load.

Mills that currently use excessive quantities of water can achieve large gains from pollution prevention. A reduction in water use of 10 to 30 percent can be accomplished by taking fairly simple measures. A walkthrough audit can uncover water waste in the form of:

- Hoses left running.
- Broken or missing valves.
- Excessive water use in washing operations.
- Leaks from pipes, joints, valves, and pumps.
- Cooling water or wash boxes left running when machinery is shut down.
- Defective toilets and water coolers.

In addition, many less obvious causes of water waste exist. These causes are presented below by subcategory, unit process, and machine type.

### 2.2.7.1 Water Consumption in Textiles

#### Subcategory

Textile operations vary greatly in water consumption. Table 2-33 summarizes the water consumption of various types of operations (14). Wool and felted fabrics processes are more water intensive than other processing subcategories such as wovens, knits, stock, and carpet.

Water use can vary widely between similar operations as well. For example, knit mills average 10 gallons of water per pound of production, yet water use ranges from a low of 2.5 gallons to a high of 45.2 gallons. These data serve as a good benchmark in determining whether water use in a particular mill is excessive.

#### By Unit Process

Water consumption varies greatly among unit processes, as indicated by Table 2-34. Certain dyeing processes and print afterwashing are among the more intensive unit processes. Within the dyeing category, certain unit processes are particularly low in water consumption (e.g., pad-batch). Low water-consuming dyeing alternatives are discussed in depth in Section 4.10, "Dyeing."

#### By Machine Type

Different types of processing machinery use different amounts of water, particularly in relation to the bath ratio in dyeing processes (the ratio of the mass of water in an exhaust dyebath to the mass of fabric). Washing fabric consumes greater quantities of water than dyeing. Water consumption of a batch processing machine depends on its bath ratio and also on mechanical factors,

Table 2-33. Water Use in Textile Processing (14)

Processing Subcategory	Water Use (gallons per pound of production)		
	Minimum	Median	Maximum
Wool	13.3	34.1	78.9
Woven	0.6	13.6	60.9
Knit	2.4	10.0	45.2
Carpet	1.0	5.6	19.5
Stock/Yarn	0.4	12.0	66.9
Nonwoven	0.3	4.8	9.9
Felted fabric	4.0	25.5	111.8

Table 2-34. Water Consumption by Unit Process (8, 11, 46, 65, 66)

Process	Water Consumption	Reference
Yarn and fabric forming	Nil	
Slashing	0.06 to 0.94	66
Preparation:		
Singeing	Nil	
Desizing	0.3 to 2.4	8, 66
Scouring	2.3 to 5.1	66
Continuous bleaching	0.3 to 14.9	66
Mercerizing	0.12	8
Dyeing:		
Beam	20	11
Beck	28	46
Jet	24	46
Jig	12	46
Paddle	35	11
Skein	30	11
Stock	20	11
Pad-batch	2	65
Package	22	46
Continuous	20	46
indigo range	1 to 6	66
Printing	3	8
Print afterwashing	13.2	8
Finishing:		
Chemical	0.6	8
Mechanical	Nil	

such as agitation, mixing, bath and fabric turnover rate (called contact), turbulence and other mechanical considerations, as well as physical flow characteristics involved in washing operations. These factors all affect washing efficiency.

In general, heating of dyebaths constitutes the major portion of energy consumed in dyeing. Therefore, low-bath-ratio dyeing equipment not only conserves water but also saves energy, in addition to reducing steam use and air pollution from boilers. Low-bath-ratio dyeing machines conserve chemicals as well as water and also achieve higher fixation efficiency. But the washing efficiency of some types of low-bath-ratio dyeing machines, such as jigs, is inherently poor; therefore, a correlation between bath ratio and total water use is not always exact.

#### 2.2.7.2 Types of Wastewater

Many sources of different types of wastewater can be found in textile operations. The most common categorization scheme for wastewater is:

Category	Example
Noncontact	Cooling
Storm	Parking lot and roof drains
Cleanup	Machines, facility, filter backwash
Process waste	Prepare, dye, finish, water-jet loom
Condensate	Boiler traps, blowdown

Each type of wastewater offers different possibilities for conservation, recycle, and reuse.

### **Noncontact Cooling Water**

Noncontact cooling water typically is isolated from all processes and, therefore, remains essentially pure after use. Cooling water includes water from water-cooled bearings and heat exchangers in dyeing machines, cooling cans on continuous ranges, and cooling towers for power boilers. In general, cooling water can be recycled directly back into the clear well or other process water supply reservoir. Most mills use excessive amounts of cooling water; therefore, this area presents significant conservation possibilities. In particular, water-cooled bearings require only a small amount of water to operate properly. A relatively simple solution is to regulate the water with flow restrictors, although this is rarely done. Another excessive use of water is cooling water left running when machines are shut down. Finding cooling water, as well as washbox water, running on dye ranges that have been shut down for months or even years is not unusual.

### **Stormwater**

Stormwater from parking lot and roof drains always should be handled in a separate discharge that is properly permitted and monitored. Stormwater sometimes is improperly connected to the process wastewater treatment system, resulting in additional load. An examination of the correlation between rainfall and treatment system influent can detect an improper connection. Stormwater should be audited on a regular basis to detect and address problems as they occur. Stormwater originating off site should not be allowed to run onto mill property and mix with onsite stormwater, resulting in external causes for stormwater permit violations.

### **Cleanup Water**

Cleanup water derives from machine maintenance and cleaning, filter backwash, facility cleaning, and other activities. The dirty water generally collects in floor drains because mills often clean the shop floors by washing them down with water, which runs into floor drains. Because of this practice, floor drains should never be plumbed into the stormwater system. Instead, floor drains should lead directly to the process wastewater treatment system. The practice of using water to

wash down the floors and letting water run into floor drains also should be eliminated from all mill procedures. Spills and other cleanup activities should be done with wet/dry shopvac vacuum cleaners wherever possible. To minimize spills, chemical handling procedures should be implemented. In particular, automated chemicals dispensing, weighing, and handling systems are useful (see Section 4.18, "Support Work Areas").

If water is used for machine and facility cleaning, it should be provided through low-volume, high-velocity nozzles, which clean more efficiently with less water. All hoses should be equipped with automatic shutoffs so that the flow automatically stops whenever the hose is not being used. A single running hose can waste 5,000 to 8,000 gallons per day. Plants often have 5 or 10 of these hoses running at different locations. Often, the shutoff valves on hoses are broken, inconveniently located, or nonexistent. Wherever possible, cleanup water should be obtained from washwater waste, not from the freshwater supply.

### **Process Water**

Wastewater from processing is the most common source of environmental concerns for textile operations. The main unit processes that produce waste are washing operations. These operations are found in almost all areas of preparation and dyeing. The details of water conservation in washing operations are discussed below.

Washing and rinsing operations are two of the most common operations in textile manufacturing that have significant potential for pollution prevention. Many processes involve washing and rinsing stages, and optimization of washing processes can conserve significant amounts of water. In some cases, careful auditing and implementation of controls can achieve wastewater reductions of up to 70 percent (67). The washing and rinsing stages of preparation typically require more water than the preparation stages (e.g., bleaching, dyeing) (67). Several typical washing and rinsing processes include:

- Drop and fill batch washing.
- Overflow batch washing.

**Table 2-35. Water Consumption for a Typical Bleach Range (66)**

Stage	Water Consumption (gallons per hour)	Percent
Saturators	550	5.0
Steamer and J boxes	150	1.4
Washers		0.0
Desize	3,700	33.5
Scour	3,100	28.1
Bleach	3,100	28.1
Dry cans	450	4.1
Total	11,050	100.0

- Continuous washing (countercurrent, horizontal, or inclined washers).

A report on water consumption for a typical continuous bleach range found that consumption was more than 11,000 gallons per hour or 0.27 million gallons per day (see Table 2-35). Washing stages accounted for 9,900 gallons per hour, or 90 percent of the total. The application of the following simple, low-technology methods of water conservation reduced water use (68):

- *Properly regulate flows:* 300 gallons per hour savings.
- *Counterflow b/each to scour:* 3,000 gallons per hour savings.
- *Counterflow scour to desize:* 3,000 gallons per hour savings.

The total water savings without process modification was 0.15 million gallons per day, or 55 percent of water use. A process modification such as a combined one-stage bleach and scour also would save 6,200 gallons of water per hour, or an additional 0.15 million gallons per day, along with energy savings (68).

### Drop-Fill Versus Overflow

In the drop/fill method of batch washing, spent washwater is drained and the machine is refilled with a fresh wash bath. The fabric or other substrate in the machine retains much of the previous bath, perhaps up to 350 percent owg. This percentage can be reduced by mechanical means (e.g., extraction, blowdown) (67). Comparison of several methods of washing after bleaching shows the benefits of countercurrent wash methods (see Table 2-36). Methods 5 and 6, which implement countercurrent washing, produce savings of 26 and 53 percent compared with the standard drop/fill method. These results are based on comparisons of washing processes that would produce the same degree of reduction of fabric impurities using computer models.

Countercurrent washing processes require the addition of holding tanks and pumps (67). The capital cost of setting up such a reuse system is low (69). Typically, the following installation costs can be expected for a system capable of recycling 75,000 gallons per day:

System	cost
Pump	\$3,000
Tank	\$14,000
Piping	\$5,000
Electrical	\$1,000
Total	\$23,000

Table 2-36. Water Use in Batch Washing (67)

Process Description	Wash/Rinse (Bath Ratio)	Water Use (gal/lb)	Percent Change From Standard
1 Standard-three-step drop/fill	1:8	1.62	-
2 Reduced bath-seven-step drop/fill	1:5	1.26	-22.2
3 Continuous overflow	1:8	2.38	+46.9
4 Continuous overflow-reduced bath	1:5	1.49	-8.0
5 Three-step drop/fill, reuse bath 2	1:8	1.19	-26.5
6 Three-step drop/fill, reuse bath 2 and 3	1:8	0.75	-53.7

Typical savings from such an installation are \$95,000 per year. In many cases, reducing wastewater also reduces the need for expensive waste treatment systems.

Brenner et al. (67) present a computer analysis that assumes complete knowledge of the state of washing systems at any given time (i.e., the amount of contaminant remaining in the fabric). In the real world, time constraints and the ability to accurately control such processes are issues. For example, in the drop/fill method, counting the number of drops and fills is relatively simple. This method facilitates matching of actual mill production processes with the computer-predicted results above.

On the other hand, controlling overflow washing is more difficult. Optimum control of overflow washing would require a knowledge of the amount of contaminant left in the substrate. In practice, this level of monitoring and control is not possible, and as a result, flow and time control are inadequate. Therefore, the overflow washing method almost always uses more water than predicted above because of a lack of control. Further information about the water-saving features of drop/fill versus overflow can be found in Brenner et al. (67) Smith (14), and Wagner (8).

### 2.2.7.3 Washwater Reuse

Many strategies can be applied for reusing washwater. Three of the most common strategies are countercurrent washing, reducing carryover, and reusing washwater for cleaning purposes.

#### Countercurrent Washing

The countercurrent washing method is relatively straightforward and inexpensive to implement in multi-stage washing processes. Basically, the least contami-

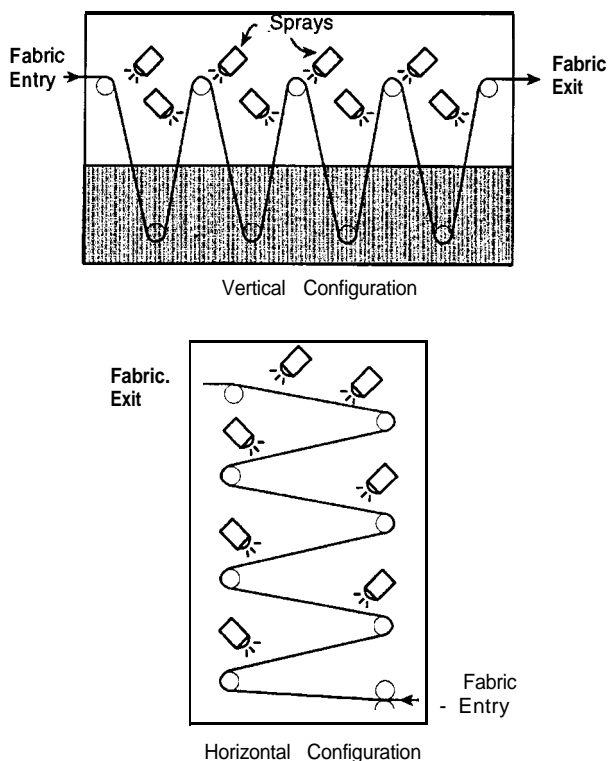


Figure 2-4. Vertical and horizontal washer configurations (11).

nated water from the final wash is reused for the next-to-last wash and so on until the water reaches the first wash stage, after which it is discharged. This technique is useful for washing after continuous dyeing, printing, desizing, scouring, or bleaching.

An important variant of the countercurrent principle is “horizontal” or “inclined” washers, as shown in Figure 2-4 (11). Horizontal or inclined washing is more efficient because of the inherent countercurrent nature of water flow within the process. The mechanical construction of an inclined or horizontal countercurrent washer has to be much better than a traditional vertical washer, however. Sloppy roll settings, weak or undersized rolls, unevenness, bends, bows, biases, bearing play, or other misalignments within the machine are much more important in a horizontal or inclined washer because the weight of water pressing down on the fabric can cause it to sag, balloon, or stretch. If properly constructed and maintained, horizontal or inclined washers can produce high-quality fabrics with much better washing efficiency and reduced water use.

#### Low Carryover

Because the purpose of washing is to reduce the amount of impurities in the substrate, as much water as possible must be removed between sequential washing steps in multistage washing operations. Water (containing contaminants) that is not removed is “carried over”

into the next step, contributing to washing inefficiency. Proper draining in batch drop/fill washing and proper extraction between steps in the continuous washing process are important. Often, 350 percent owg is carried over in typical drop/fill procedures (67). This amount can be reduced in some batch machines (e.g., yarn package dyeing, stock dyeing) by using compressed air or vacuum blowdown between washing steps.

In continuous washing operations, squeeze rolls or vacuum extractors typically extract water between steps. Equipment employing vacuum technology to reduce dragout and carryover of chemical solutions with cloth, stock, or yarn is used to increase washing efficiency in multistage washing operations. These devices are described in Section 3.19, “Pollution Prevention Through New Equipment.”

In one case history, a processor installed vacuum slots after each wash box in an existing multistage continuous washing line and was able to reduce the number of boxes from eight to three (70). Wash boxes with built-in vacuum extractors are available for purchase, as well as washers for prints that combine successive spray and vacuum slots without any bath for the fabric to pass through. Because the fabric is never submerged, bleeding, marking off, and staining of grounds is minimized, and water use decreases (70). Another washer configuration with internal recycling capabilities is the vertical counter-flow washer, which sprays recirculated water onto the fabric and uses rollers to squeeze waste through the fabric into a sump, where it is filtered and recirculated. The filter is unique, consisting of continuous loops of polyester fabric that rotate continuously and are cleaned of filtrate at one end with a spray of clean water. This construction allows for maximum removal of suspended solids from water before discharge or reuse in another process. High-efficiency washing with low water use results. Energy use decreases greatly because less water must be heated.

#### Reuse for Cleaning Purposes

In many types of operations, washwater can be reused for cleaning purposes. In printing, cleanup activities can be performed with used washwater, including (71):

- Backgray blanket washing
- Screen and squeegee cleaning
- Color shop cleanup
- Equipment and facility cleaning

A typical preparation department may also reuse washwater as follows (71):

- Reuse scour rinses for desizing
- Reuse mercerizer washwater for scouring

- Reuse bleach washwater for scouring
- Reuse water-jet loom washwater for desizing
- Recycle kier drains to saturator

#### 2.2.7.4 Water Conservation

##### Work Practices

Workers can greatly influence water use. Sloppy chemical handling and poor housekeeping can result in excessive cleanup. Poor scheduling and mix planning also can require excessive cleanup and lead to unnecessary cleaning of equipment such as machines and mix tanks. Leaks and spills should be reported and repaired promptly. Equipment maintenance, especially maintenance of washing equipment, is essential.

Inappropriate work practices waste significant amounts of water; good procedures and training are important. When operations are controlled manually, an operations audit checklist is helpful for operator reference, training, and retraining.

In one case history, a knitting mill experienced excessive water use on beck dyeing machines (20). A study of operating practices revealed that each operator was filling the becks to a different level. Some operators filled the becks to a depth of 16 inches, others as much as 24 inches. Also, the amount of water used for washing varied. Some operators used an overflow procedure, and others used drop/fill or "half baths" (repeatedly draining half of the bath, then refilling it). Inspection of the written procedures showed that the fill step simply said "fill." The wash step simply said "wash." Without training and without a specific operating procedure, operators were left to determine water use on their own.

This case may seem extreme, but even the best mills, which have well-documented production procedures, often do not have documented cleaning procedures. Cleaning operations that contribute large amounts of pollution to the total waste stream include machine cleaning, screen and squeegee cleaning, and drum washing.

##### Engineering Controls

Several areas of engineering control have been discussed, but a few additional areas deserve mention.

Every mill should have moveable water meters that can be installed on individual machines to document water use and evaluate improvements. In practice, mills rarely measure water use but rely on manufacturers' claims concerning equipment and water use. The manufacturers' estimates are useful starting points for evaluating water consumption, but the actual performance of equipment depends on the chemical system used and the substrate. Therefore, water use is situation-specific

and should be measured on site for accurate results. The water meters should be regularly maintained and calibrated.

Other important engineering controls, some of which have been discussed in other sections of this chapter, include:

- Flow control on washers.
- Flow control on cooling water (use minimum necessary).
- Countercurrent washing.
- High extraction to reduce dragout.
- Recycle and reuse.
- Detection and repair of leaks.
- Detection and repair of defective toilets and water coolers.

Machinery should be inspected and improved where possible to facilitate cleaning and to reduce susceptibility to fouling. Bath ratios sometimes can be reduced by using displacers that result in lower chemical requirements for pH control as well as lower water use. An example is shown in Figure 2-5.

##### Process Changes

Several process changes are worth mentioning in terms of water conservation. These changes are briefly noted here and covered in more detail in Sections 4.10, "Dyeing," and 4.9, "Preparation":

- Pad-batch dyeing

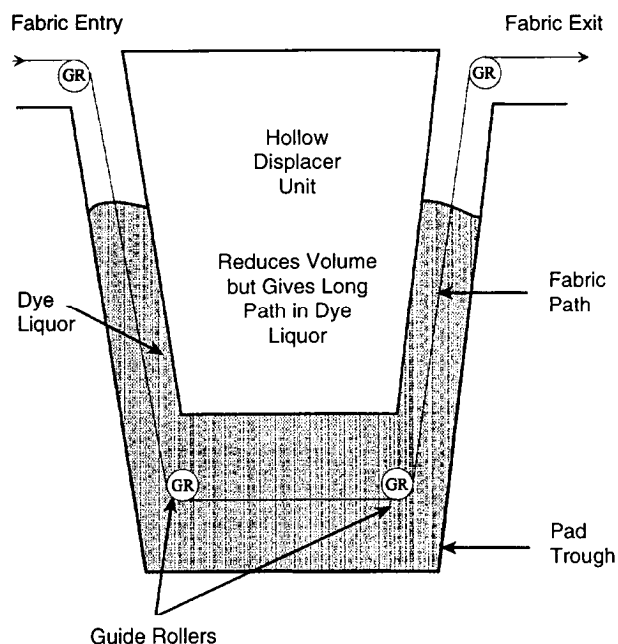


Figure 2-5. Pad with displacer.

- Processing bath reuse
- Water recycle in preparation

*Pad-Batch Dyeing.* Three major problems that face cotton dyers are water-use reduction and elimination of color and salt from dye wastewater. Fiber reactive dyes for cotton require large amounts of water for application and washoff (8).

One pollution prevention method for the application of reactive dyes is the pad-batch method. Pad-batch dyeing solves these problems without affecting the properties of fiber reactive dyes. In addition, it improves productivity and energy savings (65).

Pad-batch dyeing has been used successfully worldwide and now is being adopted in the United States (11). It is a reliable, easy-to-control method that is known for its reliable laboratory-to-production correlation on first-run dyeings.

In pad-batch dyeing, prepared fabric is padded with a solution of fiber reactive dyestuff and alkali, then stored (or batched) on rolls or in boxes and covered with plastic film to prevent evaporation of water or absorption of carbon dioxide from the air. The fabric then is batched for 2 to 12 hours. Washing can be done on whatever equipment is available in the mill.

Pad-batch dyeing offers several significant advantages, primarily cost and 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. Also, pad-batch dyeing is flexible compared with a continuous range. Either wovens or knits can be dyed in many constructions. Frequent changes of shade present no problems because reactivates remain water soluble, making cleanup easy. This method of dyeing is useful when versatility is

required. Water use typically decreases from 17 gallons per pound to 1.5 gallons per pound, a reduction of more than 90 percent (65). A full description of pad-batch dyeing can be found in Section 4.10, "Dyeing."

*Processing Bath Reuse.* Water from many processes can be renovated for reuse by a variety of methods. Several research efforts are underway. In a few operations, up to 30 percent of the treated wastewater is recycled directly back from the effluent to the raw-water intake system with no adverse effects on production. In some cases, specific types of wastewater can be recycled within a process or department. Examples are dye-bath reuse, bleach bath reuse, final rinse reuse as loading bath for next lot, washwater, countercurrent washing, and reuse for other purposes.

Several treatment strategies also are available to clean up or renovate water for reuse. Often, no treatment is needed, or a simple conventional filter step is used. The most studied methods of renovation are:

- Chlorination (72)
- Ozonation (73)
- Ultrafiltration (74)

These techniques are depicted in Figures 2-6, 2-7, and 2-8, respectively. Laboratory studies have thoroughly validated the technical and economic feasibility of each technique, but surprisingly few commercial operations have adopted these practices in the United States.

Chlorination decolorizes water by saturating it with chlorine gas in a holding tank, making it useful for dyebaths (72). The dyes, if selected properly, are destroyed without affecting other components of the bath (e.g., buffers, carriers, leveling agents, salt, dispersing agents). Of course, the waste generated and the chemicals (with associated BOD) and energy used are reduced in this

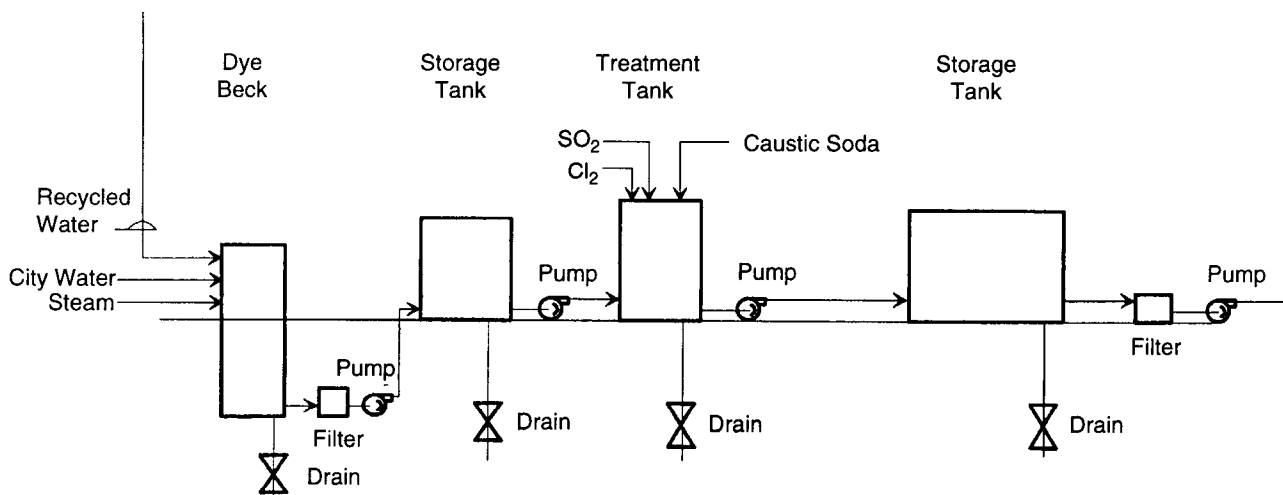


Figure 2-6. Flow diagram for chlorination water treatment system (69).

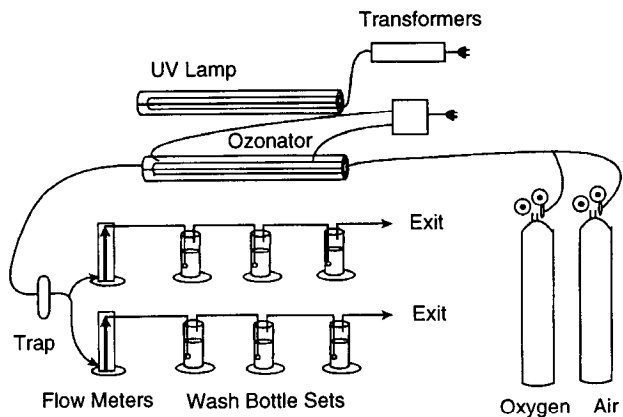


Figure 2-7. Ozone generation equipment (70).

system. One commercial operation recycles 75 percent of the dye wastewater (72). A drawback to chlorination is that it produces chloro-organics in the treated water.

Ozonation has been widely studied and, like chlorination, has been proven in repeated laboratory trials (73). The process, however, has not been widely adopted in commerce. In this method, a generator (shown in Figure 2-7) is used to produce ozone or pure singlet oxygen (73). Laboratory studies indicate that ozone is more effective than singlet oxygen, and recent studies have focused primarily on ozone (73).

Examples of the decolorization ability of ozone for CI Disperse Yellow 42, CI Basic Yellow 11, and CI Acid Red 151 are shown in Figures 2-9 and 2-10. Depletion of desirable dyebath auxiliaries is shown in Figure 2-11 (73). Ozonation has been used for multicycle repeat dyeings in laboratory settings with success and has been evaluated commercially.

Ultrafiltration has been more widely adopted than the above reactive chemical treatments. Some advantages of ultrafiltration are:

- No undesirable reaction products
- Simpler, safer operation
- Safety
- Effectiveness
- Separate recovery of chemicals and water

Ultrafiltration is essentially the same technology as that used for caustic and size recovery. Figures 2-8 and 2-12 show the basics of the ultrafiltration recovery scheme (74). Membranes are tailored to the required pore size for removal of the species of interest (see Figure 2-13) (74). Ultrafiltration can produce 95-percent water recovery in commercial practice (74). These systems have been widely adopted in commerce and have proven invaluable. Payback for dyebath recovery is estimated

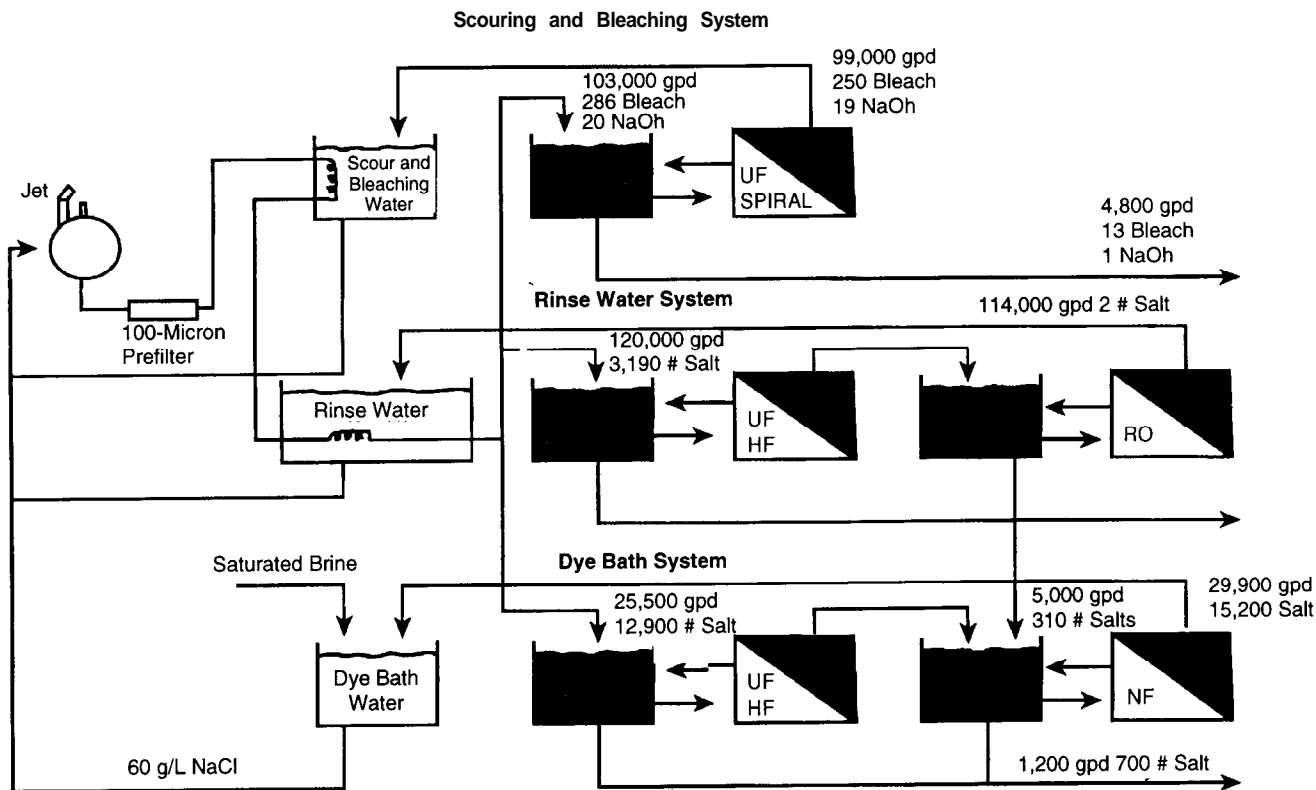


Figure 2-8. Recycle of jet dyeing machine flows using ultrafiltration (71).

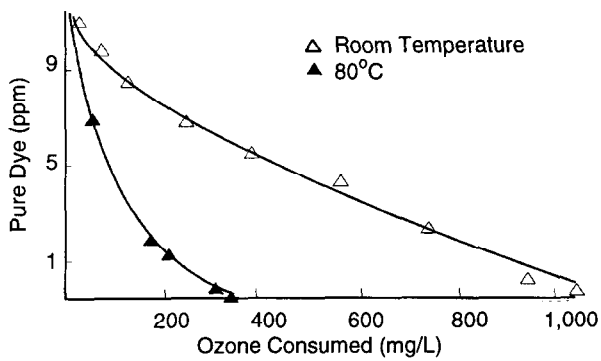


Figure 2-9. Ozone decolorization of Disperse Yellow 42 (70).

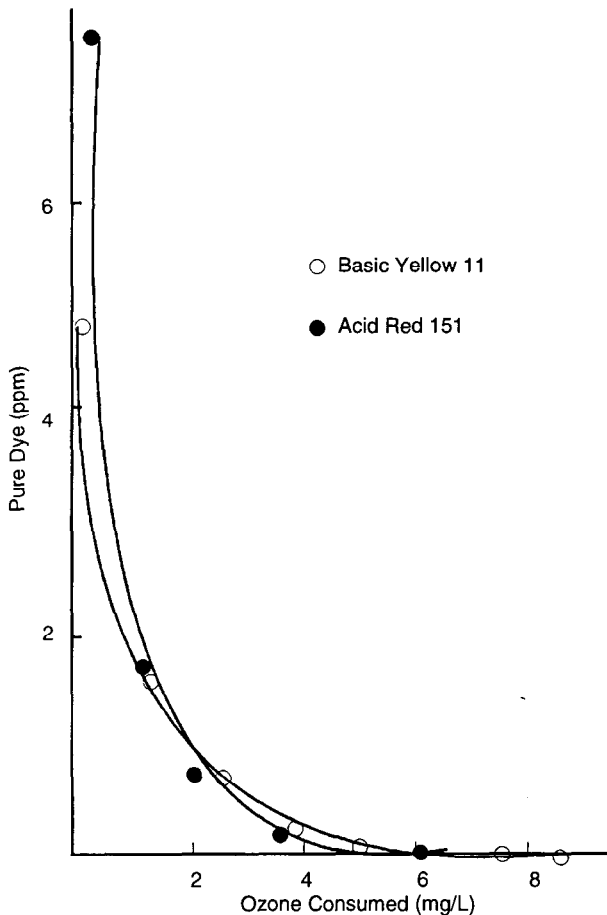


Figure 2-10. Dye decolorization by ozone (70).

to be 1.5 years, and shade reproducibility is better than the reactive methods listed above (74).

### Dyebath Reuse

In the 1960s, about 10 to 16 percent of textile wastewater was reclaimed or recycled (14). Recent improvements, including dyebath reuse, have dramatically increased the potential for reuse, with corresponding

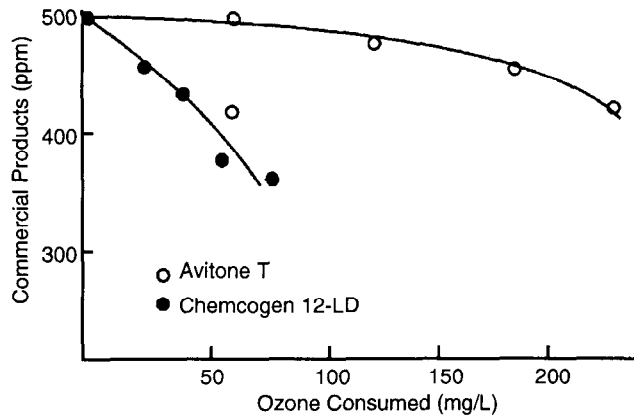


Figure 2-11. Ozone oxidation of auxiliaries (70).

cost savings and waste reduction. No current study of water reuse in textile mills has been published. Dyebath reuse, one pollution prevention method for water conservation, has been shown to reduce flow, BOD, and COD loadings by up to 33 percent (14). Dyebath reuse also shows a return on investment in the form of dye, chemical, and energy savings that pretreatment does not. Savings, installation costs, and operating expenses are site-specific, but a typical payback period is 13 to 20 months (14). This is discussed in detail in Section 4.10.6.5.

### Bleach Bath Reuse

Cotton and cotton blend preparation (e.g., desizing, scouring, bleaching) are performed using continuous or batch processes and usually are the largest water consumers in a mill. Continuous processes are much easier to adapt to wastewater recycle/reuse because the waste stream is continuous, shows fairly constant characteristics, and usually is easy to segregate from other waste streams.

Waste-stream reuse in a typical bleach unit for polyester/cotton and 100-percent cotton fabrics would include:

- Recycling J-box and kier drain wastewater to saturators.
- Using countercurrent washing.
- Recycling continuous scour washwater to batch scouring.
- Recycling washerwater to backgray blanket washing.
- Recycling washerwater to screen and squeegee cleaning.
- Recycling washerwater to color shop cleanup.
- Recycling washerwater to equipment and facility cleaning.
- Reusing scour rinses for desizing.
- Reusing mercerizer washwater for scouring.

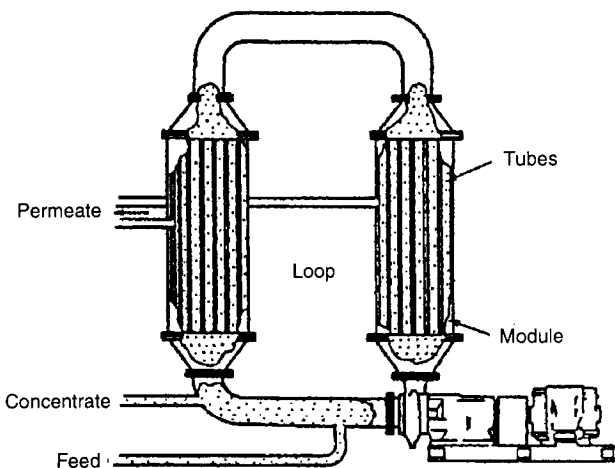


Figure 2-12. Typical membrane configuration for ultrafiltration (72).

- Reusing bleach washwater for scouring.
- Reusing water jet loom washwater for desizing.
- Recycling kier drains to saturators.

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

Batch scouring and bleaching are less easy to adapt to recycling of waste streams because streams occur in-

termittently, drains generally go into pits and are not easily segregated, and batch preparation steps frequently are combined. With appropriate holding tanks, however, bleach bath reuse can be practiced in a similar manner to dyebath reuse, and several pieces of equipment are now available that have the necessary holding tanks (67). The spent bleach bath contains all of the alkali and heat necessary for the next bleaching operation (67). Peroxide and chelates must be added to reconstitute the bath. Like dyebath reuse, the number of reuse cycles in bleach bath reuse is limited by impurity buildup. The main impurities are metals, such as iron, that can interfere with the bleaching reaction.

### Continuous Knit Bleaching

New types of rope bleaching units for knits featuring 6- to 12-stage jet transport systems have made continuous bleaching of most knit styles possible (70). These units were introduced in the late 1970s and typically produce 40 pounds per minute of knit fabric or more than 1 million pounds per month based on a three-shift, 6-day operation. These machines have become very popular with large knit processors because of their flexibility and ability to conserve energy, water, and chemicals. They also have complete countercurrent capabilities built in. These units are being promoted for use in after-washing fiber reactive and other types of dyes (e.g., after pad-batch dyeing) in addition to use as continuous knit preparation ranges. This is discussed further in Section 3.19, "Pollution Prevention Through New Equipment."

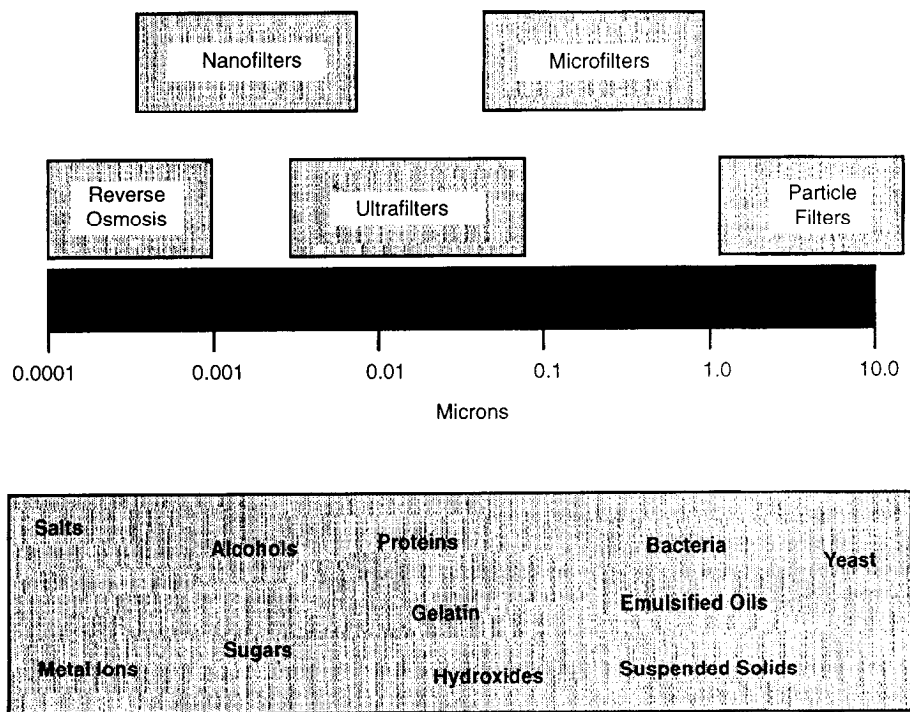


Figure 2-13. Tangential filtration (71).

### **Final Rinse Reuse as Loading Bath for Next Lot**

One simple technique that saves water and, in some cases, BOD loading is to reuse the final bath from one dyeing cycle to load the next lot. This technique works well in situations where the same shade is being repeated or where the dyeing machine is fairly clean.

A good example of this technique is acid dyeing of nylon hosiery. The final bath usually contains an emulsified softener that exhausts onto the substrate, leaving the emulsifier in the bath. This technique can serve as the wetting agent for loading the next batch, thus saving the water, heat and wetting agent, and associated BOD.

### **2.2.7.5 Waterless Alternatives**

Several waterless processing methods deserve comment. The most widely practiced method is mechanical finishing, which is described in Section 4.12, "Finishing."

In the area of preparation and dyeing, waterless processes are based on supercritical carbon dioxide fluid (SCF) technology. These processes use no water, and drying is simply a matter of letting the carbon dioxide flash off, which happens immediately upon releasing the supercritical pressure. One advantage of these systems is that commercially available disperse dyes for polyester can be used, so no special colorants have to be developed. Waterless processes are being used only in laboratories and pilot plants at this time, but they deserve attention.

Waterless mercerization can be accomplished by the use of liquid ammonia, which is recovered and reused. Liquid ammonia mercerization is effective and practiced on a wide scale commercially. One promising area of research at this time is the use of ammonium thiocyanate in the ammonia bath to elevate the boiling point of the liquid ammonia to room temperature, reducing the need for expensive cooling systems to run the liquid ammonia mercerization process.

Another laboratory development is the use of powder colorants and xerographic printing techniques for waterless textile coloration processes.

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