

Identification and Reduction of Pollution Sources in Textile Wet Processing

by

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Editor's Note

We revised the covers and this page to reflect organizational changes in state government. The title and text have not been changed from the original 1986 printing.

THE POLLUTION PREVENTION PROGRAM

The Pollution Prevention Program provides free technical assistance to North Carolina industries and municipalities on ways to reduce, recycle and prevent wastes before they become pollutants. This non-regulatory program addresses water and air quality, toxic materials, and solid and hazardous waste. Designated as the lead agency in waste reduction, the Program works in cooperation with the Solid Waste Management Division and the Governor's Waste Management Board. The services and assistance available fall into the following categories:

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Specific Information Packages. The staff can prepare facility or waste-stream-specific waste reduction reports for industries and communities. Information provided by the facility is used to identify cost-effective waste reduction options. A short report detailing these options is provided along with references, case studies, and contacts.

On-site Technical Assistance. The staff can provide comprehensive technical assistance through facility visits. During an on-site visit, detailed process and waste stream information is collected. The information is analyzed, and a series of waste reduction options are identified. A report is prepared detailing these options and includes literature, contacts, case studies, and vendor information.

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For information or technical assistance contact:

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IN TEXTILE WET PROCESSING

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1.0 INTRODUCTION

This document identifies pollutant sources in textile wet processing and suggests some management strategies by which source reduction can be accomplished. Reduction strategies are broadly categorized as either:

- . Processing Alternatives
- . Recovery/Recycle/Reuse

Examples of source reduction are usually very site-specific; therefore, the application of the ideas presented here must be flexible. In many cases, a commitment to reduction of pollution sources can also lead to cost and quality improvements for a manufacturer.

1.1 Textile Waste Sources

There have been many, traditional studies of textile waste water characteristics [1-71. These data characterize certain types of textile wastes, and they are well summarized in a reference document published by CRC 181. However, these studies, in many cases, fail to accurately characterize the waste streams from modern textile operations in the southeastern U.S.A. More recent documents, published by EPA [9,10] give a more accurate description of textile wastes water streams. Table 1.1-I through 1.1-V show data for these studies.

An important question for any textile mill which discharges into a publicly owned treatment works (POTW) is the comparison of these typical waste data with pretreatment specifications imposed on the industrial discharges by

Table 1.1-I

Water Usage and Mill Wastewater Discharge - Summary of Historical Data [10]

Subcategory	Water usage, l/kg		(gal/lb) of production		Discharge, cu m/day (MGD)		No. of mills	
	Min		Med.	Max.	median mill			
1. Wool scouring	4.2	(0.5)	11.7	(1.4)	77.6	(9.3)	103 (0.051)	12
2. Wool finishing	110.9	(13.3)	283.6	(34.1)	657.2	(78.9)	1892 (0.500)	15
3. Low water use processing	0.8	(0.1)	9.2	(1.1)	140.1	(16.8)	231 (0.061)	13
4. Woven fabric finishing								
a. Simple processing	12.5	(1.5)	78.4	(9.4)	275.2	(33.1)	636 (0.168)	48
b. Complex processing	10.8	(1.3)	86.7	(10.4)	276.9	(33.2)	1533 (0.405)	39
c. Complex processing plus desizing	5.0	(0.6)	113.4	(13.6)	507.9	(60.9)	636 (0.168)	50
5. Knit fabric finishing								
a. Simple processing	8.3	(0.9)	135.9	(16.3)	392.8	(47.2)	1514 (0.400)	71
b. Complex processing	20.0	(2.4)	83.4	(10.0)	377.8	(45.2)	1998 (0.528)	35
c. Hosiery products	5.8	(0.7)	69.2	(8.3)	289.4	(34.8)	178 (0.047)	57
6. Carpet finishing	8.3	(1.0)	46.7	(5.6)	162.6	(19.5)	1590 (0.420)	37
7. Stock and yarn finishing	3.3	(0.4)	100.1	(12.0)	557.1	(66.9)	961 (0.254)	116
8. Nonwoven manufacturing	2.5	(0.3)	40.0	(4.8)	82.6	(9.9)	389 (0.100)	11
9. Felted fabric processing	33.4	(4.0)	212.7	(25.5)	930.7	(111.8)	564 (0.149)	11

Table 1.1-II

Raw Waste Concentrations - Conventional and Nonconventional Pollutants
Historical Data - Median Values [10]

Subcategory	BOD (mg/l)	COD (mg/l)	COD — BOD	TSS (mg/l)	O&G (mg/l)	Phenol (µg/l)	Chromium (µg/l)	Sulfide (µg/l)	Color APHA Units
1. Wool scouring	2270	7030	3.1	3310	580	†	†	†	†
2. Wool finishing	170	590	3.5	60	†	†	†	†	†
3. Low water use processing	293	692	2.4	185	†	†	†	†	†
4. Woven fabric finishing									
a. Simple processing	270	900	3.3	60	70	50	40	70	800
b. Complex processing	350	1060	3.0	110	45	55	110	100	†
c. Complex processing plus desizing	420	1240	3.0	155	70	145	100	†	†
5. Knit fabric finishing									
a. Simple processing	210	870	4.1	55	85	110	80	55	400
b. Complex processing	270	790	2.9	60	50	100	80	150	750
c. Hosiery products	320	1370	4.5	80	100	60	80	560	450
6. Carpet finishing	440	1190	2.7	65	20	130	30	180	490
7. Stock and yarn finishing	180	680	3.77	40	20	170	100	200	570
8. Nonwoven manufacturing	180	2360	13.1	80	†	†	†	†	†
9. Felted fabric processing	200	550	2.75	120	30	580	†	†	†

†Insufficient data to report value.

Table 1.1-III

Raw Waste Loads - Conventional and Nonconventional Pollutants
 Historical Data - Median Values [10]

Subcategory	BOD	COD (kg/kkg)	TSS	O&G	Phenol	Chromium (g/kkg)	Sulfide
1. Wool scouring	41.8	128.9	43.1	10.3	†	†	†
2. Wool finishing	59.8	204.8	17.2	†	†	†	†
3. Low water use processing	2.3	14.5	1.6	†	†	†	†
4. Woven fabric finishing							
a. Simple processing	22.6	92.4	8.0	9.1	8.2	4.3	7.6
b. Complex processing	32.7	110.6	9.6	3.8	7.7	2.6	12.5
c. Complex processing plus desizing	45.1	122.6	14.8	4.1	13.1	20.9	†
5. Knit fabric finishing							
a. Simple processing	27.7	81.1	6.3	4.0	8.7	7.8	13.0
b. Complex processing	22.1	115.4	6.9	3.5	12.0	4.7	14.0
c. Hosiery products	26.4	89.4	6.7	6.6	4.2	6.4	23.8
6. Carpet finishing	25.6	82.3	4.7	1.1	11.3	3.4	9.4
7. Stock and yarn finishing	20.7	62.7	4.6	1.6	15.0	12.0	27.8
8. Nonwoven manufacturing	6.7	38.4	2.2	†	†	0.5	†
9. Felted fabric processing	70.2	186.0	64.1	11.2	247.4	†	†

†Insufficient data to report value.

Table 1.1-IV

Raw Waste Concentrations - Conventional and Nonconventional Pollutants
Results of Field Sampling Program [10]

Mill Subcategory	BOD (mg/l)	COD (mg/l)	TSS (mg/l)	O&G (mg/l)	Phenol (µg/l)	Chromium (µg/l)	Sulfide (µg/l)	Color APHA Units	pH Units
Wool scouring	1900	6100	2300	-	-	10	500	2200	10.4
Wool scouring	5000	24000	87000	1100	220	220	-	-	7.8
Wool finishing	450	1700	160	90	190	190	6000	2000	10.7
Wool finishing	330	1100	70	160	880	880	1100	1000	9.2
Low water use processing	-	1900	-	-	-	-	-	-	-
Low water use processing	-	720	15	80	10	80	1000	-	-
					4	-	ND	10	6.9
Woven fabric finishing									
Simple processing	50	-	55	-	4	20	1000	500	9.0
Simple processing	400	1100	200	-	8	90	200	-	-
Complex processing	500	500	30	-	70	70	7600	1300	9.5
Complex processing	450	1700	90	-	280	280	1000	1500	10.5
Complex processing	-	2000	-	-	150	150	1000	-	-
Complex processing	1500	-	500	20	-	-	-	-	11.2
Complex processing	600	1600	15	-	-	-	-	-	9.3
Complex plus desizing	290	320	40	-	-	-	20	1200	10.0
Complex plus desizing	20	2700	50	-	70	70	1000	250	10.0
Complex plus desizing	400	1500	110	-	55	55	5600	3200	10.0
Complex plus desizing	560	1700	70	-	65	65	1000	40,000	10.0
Complex plus desizing	440	800	50	-	75	75	5200	2600	10.2
Complex plus desizing	350	800	20	-	55	55	2500	500	10.0

Notes: A dash indicates that analyses were not performed.
ND indicates "Not Detected".

Table 1.1-IV (continued)

Mill Subcategory	BOD (mg/l)	COD (mg/l)	TSS (mg/l)	O&G (mg/l)	Phenol (µg/l)	Chromium (µg/l)	Sulfide (µg/l)	Color APHA Units	pH Units
Knit fabric finishing									
Simple processing	-	-	6	-	230	-	6000	300	10.0
Simple processing	200	580	25	-	740	6	2100	150	9.2
Simple processing	240	780	20	320	940	20	750	740	10.2
Complex processing	220	560	25	-	110	1	9200	250	10.0
Complex processing	-	730	25	-	1	10	1000	-	-
Hosiery products	-	880	20	180	-	660	1800	820	7.5
Hosiery products	-	820	180	340	-	8	ND	220	9.1
Hosiery products	-	2900	95	630	-	-	ND	270	6.4
Carpet finishing	200	1300	40	-	30	4	1000	300	11.0
Carpet finishing	-	940	-	-	45	25	1000	-	-
Carpet finishing	180	740	20	-	-	55	-	-	-
Stock and yarn finishing	1100	1300	30	-	40	10	1400	1400	10.5
Stock and yarn finishing	380	1100	20	-	40	3	4500	1300	7.4
Stock and yarn finishing	120	460	35	-	65	25	1000	10,000	10.5
Stock and yarn finishing	-	-	-	-	-	650	-	-	-
Stock and yarn finishing	-	640	125	210	-	-	ND	310	6.2
Nonwoven manufacturing	-	340	-	-	45	10	1000	-	-
Nonwoven manufacturing	-	220	35	-	-	4	ND	140	9.4
Nonwoven manufacturing	-	480	15	-	-	-	ND	35	6.3
Felted fabric processing	-	1100	40	-	-	-	1200	190	7.3

Notes: A dash indicates that analyses were not performed.
 ND indicates "Not Detected".

Table 1.1-XXI

Raw Waste Concentrations - Conventional and Nonconventional Pollutants
Summary of Historical and Field Sampling Data [10]

Subcategory	BOD (mg/l)	COD (mg/l)	TSS (mg/l)	O&G (mg/l)	Phenol (µg/l)	Chromium (µg/l)	Sulfide (µg/l)	Color APHA units
1. Wool scouring	2300	7000	3300	600	†	(120)	(500)	(2200)
2. Wool finishing	170	600	60	†	(120)	(500)	(3500)	(1500)
3. Low water use processing	290	690	180	(80)	†	(4)	†	(10)
4. Woven fabric finishing								
a. Simple processing	270	900	60	70	50	40	70	800
b. Complex processing	350	1100	110	50	50	110	100	(1400)
c. Complex processing plus desizing	420	1240	150	70	150	100	(1700)	(1900)
5. Knit fabric finishing								
a. Simple processing	210	870	50	80	110	80	55	400
b. Complex processing	270	790	60	50	100	80	150	750
c. Hosiery products	320	1370	80	100	60	80	560	450
6. Carpet finishing	440	1190	70	20	130	30	175	490
7. Stock and yarn finishing	180	680	40	20	170	100	200	570
8. Nonwoven manufacturing	180	2360	80	(60)	(40)	(10)	†	(90)
9. Felted fabric processing	200	550	120	30	(580)	†	(1200)	(200)

†Insufficient data to report value.

the POTW. Typical limitations for textile mills discharging into municipal POTW's are:

BOD	300 ppm
TSS	250 ppm
PH	6-9 or 6-10
NH ₃ as N	40 ppm
P	varies
Metals	varies
Temperature	105 ^{0F} to 140 ^{0F} max
Oil and grease	100 ppm
Solid waste screens	1/2" max

In most cases, some types of pretreatment or process modification and/or source reduction are required to meet the above specifications. This document contains surveys of source reduction technologies, case histories, and ideas that allow a textile mill to accomplish specific results in the area of source reduction. It is important for the POTW and the textile processor to understand each other, however, before making major source modifications. Specifically, each must consider important factors like aquatic toxicity in addition to BOD and other specified parameters. These factors need to be kept in balance. Data are available which show that many industrial and POTW effluents have aquatic toxicity [11]. The sources and types of such aquatic toxicity are discussed in Section 2.2. of this document. One example of toxicity is residual surfactants which have survived treatment; i.e., the surfactants (especially the hydrophobic parts) are not fully degraded by biological processes used to treat the wastewater. It is well known that branched and/or aromatic surfactant structures are less degradable, have lower BODs and higher aquatic toxicity due to less degradation than similar linear structures. For example, branched-chain decyl alcohol ethoxylates will

have lower BODs but higher toxicity in treated wastes. Thus, a requirement by a POTW for a textile mill to meet the typical 300 ppm BODs requirement may well result in the mill's selection of chemical specialties based on less degradable surfactants which will increase the aquatic toxicity of the POTW'S treatment effluent and which can cause other operational problems such as foaming, bulking and floating solids.

One important factor to keep in mind concerning these POTW criteria for industrial discharges is that local POTW can set any reasonable level for industrial discharges (within federal standards). The often-used limit of 300 ppm for BODs and 6 to 9 for pH are not required by the North Carolina Division of Environmental Management nor any federal agency, and these can be adjusted by the POTW for individual discharges. Furthermore, the North Carolina Division of Environmental Management does not suggest any specific BOD, PH, or other limitations. Each situation must be evaluated on its own merits. Therefore, a mill that discharges to a POTW should make every effort to inform the POTW about specific needs for limitations prior to making product/process modifications that involve tradeoffs such as BOD/toxicity, BOD/metals, etc. In most cases involving proprietary chemical specialties, the mill cannot know specifically the chemical constitution of its raw materials. Thus an inflexible approach to BOD compliance parameters by selecting products, for example, with the lowest available BOD, may well be counterproductive. If the POTW can accept BODs above the minimum, they should accommodate the mill whenever possible. However, even in spite of the specific EPA warnings against BOD/toxics tradeoffs [22], municipalities tend to be rather inflexible concerning their established standards, and variances are the exception rather than the rule.

A related situation can occur when a mill reduces its water consumption through the types of conservation methods discussed in Section 3.3. This lowering of water use raises the concentration of chemicals (BOD, NH₃ as N, etc.) in the waste stream. In these cases, the POTW should strongly consider variances to reward (and not punish) the mill's attempt to reduce hydraulic loading by water conservation. Strangely, conservation of water sometimes can result in real problems for a mill because of increased concentrations of waste. Alternative pretreatment specifications based on loading, not concentration, should be considered in such cases. In summary, the mill and the POTW must understand each other and work together toward the common goal of pollution reduction.

Mills that treat their own waste have much more flexibility, however. Source reduction practices like those suggested here can save many dollars in waste treatment system expansion, upgrading, and operation.

1.2 General Approaches to Textile Waste Reduction

There are many strategies which a manufacturer might use for reducing potential pollution sources. Some of these which are appropriate to textile wet processing are described from a mill process point of view in this document. This includes literature reviews as well as mill experiences with various situations. For most cases, the results which can be obtained are site-specific, and each manufacturing process must be evaluated on its own merit as a separate situation. Some ideas that have been used commercially for pollution source management which will be discussed in this document are as follows:

Preparation

Recovery systems
Waste stream reuse
Chemical substitutions
Alternative processing

Dyeing

Reconstitution/reuse of dyebaths
Chemical substitution
Alternative processes

Finishing

Reuse
Substitution
Alternative processes

General

Waste characterization
Raw materials
The fate of processing chemicals
Equalization

Previous studies [1-7] have included textile waste analyses, but most of these are obsolete and many were done outside the U.S.A. They typically include wastes from wool processing as the primary type of textile wastes, which is not characteristic of current commercial practice in the U.S.A. This document is related primarily to cellulosics and synthetics such as polyester, acrylic, nylon, and blends. Unfortunately, many practicing engineers rely heavily on these inappropriate studies [1-7].

In order for a textile manufacturer to use process modifications, reuse, recovery, and other control strategies to accomplish pollution source reduction, he must first identify the major processes contributing to the undesirable waste stream. Previous characterizations of textile waste streams have been widely cited in modern reviews [8]. However, little or no documentation exists which identifies specific process and/or raw material

precursors of undesirable waste stream components. For textile mills, several estimations can be made concerning such sources and precursors. Of primary concern, especially for mills that discharge into POTWs are TSS, pH, metals, toxicity, and BOD. Usually, TSS levels of 100 ppm or less are achieved by either in-process removal of lint, vibrating screen filters, or other primary control technologies. This is usually adequate to provide TSS levels of 50 ppm or less.

However, control of toxic waste, BOD, and pH is not so easy. In particular, pretreatment systems to control these are large and expensive, and have little or no payback other than the elimination of sewer surcharges. Waste reduction strategies presented here can reduce significantly the cost of operating a required pretreatment system or eliminate its need altogether. The typical limits that must be met in city sewer ordinances are shown in Section 1.1.

2.0 SOURCES OF WASTE

It is important for each source of waste to be carefully identified for a textile processing operation. This can be done by 1) inventory control and knowledge of potential pollutants in purchased products or 2) process analysis.

This section will concentrate on the identification of pollutant sources in textile processing. Specific types of pollutants that will be considered in detail are:

- . BOD
- . Toxicity
- . Acidity/Alkalinity/pH
- . Metals
- . Air Emissions

2.1 Sources of BOD

In order to identify processes and their contributions to BODs in waste streams, each textile wet processing step will be listed with appropriate general comments concerning the potential BOD contributions (see Table 2.1-I). The BOD values of products given in tables represent data that have been previously published. Extensive lists of BOD data of textile chemical specialties are circulated privately, but cannot be published because they are proprietary.

Certain chemical manufacturers will share the data on their products freely while others will not. One way for a mill to overcome this problem, if it arises, is to insist that BOD, COD, and other data be presented, along with other essential data (MSDS) as part of product evaluation prescreening procedures as discussed in Section 3.4.

Table 2.1-I

BOD Contributions of Various Textile Processes

Process	#BOD per 100# fabric
Singe (woven only)	None
Desize (woven only)	
Enzyme/starch	67
Starch/CMC mix	20
PVOH or CMC only	- 0
Scouring	40-50
Bleaching	
Peroxide	3-4
Hypochlorite	8
Mercerizing	
(no caustic recovery)	15
(with caustic recovery)	6
Heatsetting (synthetic only)	- 0

2.1.1 Preparation

Preparation processes include the following typical BOD contribution:

2.1.1.a Desizing

Desizing of woven fabrics is the first major wet processing step (except for possibly singeing, which does not produce a significant waste water stream). There are many types of sizing materials available, and most commercial sizes are mixtures.

The BOD values of size materials are listed in several sources and are given in Table 2.1.1.a-I.

The general trends in Table 2.1.1.a-I show that starch sizes will have BODs of 500,000 to 600,000 ppm; alginates and modified starches, 100,000 to 500,000 ppm; and synthetic sizes (PVOH, CMC, PVAc), about 10,000 to 30,000. In addition, starches are generally removed with enzymes which themselves have BODs typically over 10,000 ppm. The removal of CMC, PVOH, and PVAc and other synthetic sizes is usually accomplished with hot water and perhaps alkali so that the removal system itself does not normally contribute to BOD load. Furthermore, synthetic sizes can generally be recovered from waste streams (see Section 4.1.2). Thus a change from starch to synthetic sizes can give BOD reduction from this major source of over 90%. In a typical operation, this would be about 50% of the total BOD load from preparation for woven fabrics (but not knits).

Table 2.1 .1 .a-1

BODs of Size Materials [5, 14, 15, 16]

Size material	ppm BOD
Ahco nylon wax size	340,000
B-2 gum (starch dextrins)	610,000
Brytex gum 745 (starch)	610,000
Carboxymethyl cellulose (CMC)	30,000
Elvacet (polyvinyl acetate, PVAc)	10,000
Elvanol 72-60 (polyvinyl alcohol, PVOH)	10,000-16,000
Globe Easyflow starch	650,000
Hydroxyethyl cellulose (HEC)	30,000
KD gum (starch)	570,000
Keofilm No. 40 (starch)	50,000-550,000
Morningstar starch	470,000
Nicol starch	570,000
Pearl (cornstarch, No. 173 and PT)	500,000
Penrod Gum 300 (hydroxy starch ether)	360,000
RTC gum (starch-urea)	120,000
Starch No. 450	460,000
Sodium alginate	360,000
Wheat starch	550,000
Ambertex M (starch paste)	20,000

Other factors to consider are auxiliary components of size mixtures that are commonly used in commerce. Components of commercial sized size formulations include:

<u>Component</u>	<u>% of total size mix solids</u>
Size (starch, CMC, PVOH, PVAc, etc.)	85-90%
Humectant (urea, diethylene glycol, etc.)	2-5%
Lubricant (wax or oil)	2-5%
Antistat	0.5%
Biocide	varies
Glycerine (improves adhesion for spun yarns)	2.0%
Wetter (improves penetration for filament)	0.1%

The size material itself may be a single component or mixture of components and will usually constitute 85-90% of the total solids in the size mixture.

Other commonly used components have the following BOD [15]:

<u>Materials</u>	<u>BOD (ppm)</u>
Urea	90,000
Glycerine	640,000
Waxes	100,000 to 1,500,000
Oils	100,000 to 1,500,000
Antistat	varies widely
Bactericide	test fails
wetter/penetrant	varies widely
Diethylene glycol	60,000
Wetters	varies widely

Each of these additional materials will, of course, contribute to the total BOD of waste streams from sizing/desizing operations.

2.1.1.b Scouring

Scouring processes are for removal of oils, waxes and other impurities. This is generally accomplished by either emulsification of synthetic oils and waxes, or by saponification of naturally occurring impurities (triglycerides).

Typically, scouring wastes contribute a large portion but less than 50% of BOD loads in waste streams from preparation processes.

Synthetic oils and waxes include winding emulsions, paraffin wax, knitting oil, coning oil, and other lubricants. These materials have significant BOD themselves, and the emulsifiers used to remove and suspend them in preparation also contribute. The BOD values of several such materials are presented in Table 2.1.1.b-I.

The data in Table 2.1.1.b-II shows that the BODs of surfactants vary widely, the highest being natural soaps which are saponification products of triglycerides (glycerol esters of naturally occurring long-chain fatty acids) such as lauric and oleic acid. The fatty acids and/or their salts are sometimes used as scouring agents in alkaline medium. These typically have BODs over 1 million ppm. Synthetic detergents have lower BODs.

However, the use of lower BOD products per se is not always desirable. For example, branched alcohol ethoxylates are known to be less degradable, therefore, have lower 5-day BOD than linear alcohol ethoxylates. In a typical activated sludge waste treatment system, therefore, these branched materials will not be degraded to the same degree as their linear counterparts: They will pass through to a greater extent and therefore increase the aquatic toxicity of treated effluent. Toxic components of effluents are of great concern currently (see Section 2.2). These materials can also affect treatment system performance adversely.

2.1.1.c Bleaching (BOD)

The BOD contribution from continuous bleaching operations is fairly low, less than 5% [2] of the total textile mill BOD, typically. In addition, many synthetic fibers and blends require little or no bleaching compared with

Table 2.1 .1 .b-I

BODs of Detergents and Surfactants [11,14,15]

Product	5 day BOD (ppm)
All detergent	40,000
Dreft detergent	49,000
Igepal talkyl phenol EO)	40,000
Igepon AP-78 (sodium isothionate oleate)	1,210,000
Igepon T-77 (sulfonamide)	1,660,000
Isodecyl alcohol 6 EO (Epilsophogene DA 63)	100,000
Ivory Snow	1,220,000
Lauryl sulfate	1,250,000
Merpol B (alcohol sulfate)	440,000
Neodol 25-3-S (alcohol EO sulfate)	570,000
Neodol 25-7 (12-15 C alcohol/7 EO)	450,000
Neodol 45-7 (14-15 C linear alcohol/7 EO)	650,000
Nonyl phenol 10 EO (Igepal C0630)	24,000
Orvus K (ammonium lauryl sulfate)	1,560,000
Parval (fatty amide soap)	50,000
Rome soap flakes	1,220,000
Sandopan TLF (sulfonated fatty amide)	50,000
Santomerse 3 (sodium alkyl aryl sulfonate)	90,000
Saponite (solvent scour)	830,000
Sulfanol KB (sodium alkyl aryl sulfonate)	0
Sulfonated castor oil	520,000
Sulfonated vegetable oil	590,000
Syndet (amide detergent)	120,000
Tallow	1,520,000
Tallow soap	550,000
Tergitol 15-S-7 (11-15 C secondary alcohol 7 EO)	150,000
Triton 770 (alkylaryl polyester sulfate)	90,000
Triton 771 (polyester sulfate)	50,000
Triton X-114 (isooctyl phenol EO)	100,000
BP solvent	940,000
Duponol C (lauryl sulfate)	1,250,000
Duponol D (alcohol sulfate)	450,000
Duponol RA (Wetter)	330,000
Duraline (solvent scour)	160,000
Ethofat C/15 (fatty acid/E01)	1,000,000
Ethofat C60 (fatty acid/ EO)	220,000
Ethomid HT/15 (amide/E01)	1,000,000
Ethomid HT/60 (amide/E01)	90,000
Extol XP Special	700,000
Iberscour	530,000
Igepol CA-630 (wetter)	130,000
Igepol CA conc.	70,000
Iversol (solvent scour)	600,000

Table 2.1.1.b-I (continued)

Product	5 day BOD (mm)
Kierpine Extra (sulf. oils)	610,000
Kreelon 8D (sodium alkyl aryl sulfonate)	50,000
Kreelon 8G (sodium alkyl aryl sulfonate)	230,000
Kyro AC (fulling)	120,000
Merpol B (alcohol sulfate)	440,000
Monotone A	200,000
Naccosol A	20,000
Nacconol NR	0 to 40,000
Nacconol NRSE	0
Nekal NF	120,000
Nevtronyx 60D	0
Orvas Neutral Granules	30,000
Parval (fulling)	50,000
Pine Oil	1,080,000
Pluronic F68 (polyglycol ether)	120,000
Rinsol	720,000
Sandozol KB (sulf. vegetable oil)	150,000
Solpinol Special	700,000
Solvent A	250,000
Solvent GTS	410,000
Solvent T	250,000
Solvex	10,000
Special Textile Flakes	1,120,000
Strodex	120,000
Supertex E	250,000
Syndet	120,000
Syntholite #100	100,000
Triton 770	90,000
Triton W30	500,000
Ultrawet DS	0
Ultrawet 35K	0
Xylol Scour Special	420,000

fabrics and yarns of pure cotton or wool. Thus, current commercial practice is such that the BOD from bleaching operations is not a critical factor in overall BOD production. However, wetting agents and other auxiliaries are sometimes used which can contribute to BOD load and toxicity. Also, some mills use a modified procedure in which scour and bleach may be combined. Thus, the overall impact of process control and source reduction in bleaching is site-specific.

2.1.1.1.d Other Preparation Processes (BOD)

Other preparation processes include heatsetting (synthetics), mercerizing (cotton), and singeing. These, like singeing and bleaching, contribute relatively little to waste stream BODs compared to desizing and scouring.

2.1.2 Dyeing

Dyeing processes vary greatly in the amount and type of wastes produced. Many details of exhaust dyeing processes are discussed in Section 6 of this document on dyebath reuse. Continuous dyeing methods including pad batch dyeing generally use much lower quantities of chemicals and water than exhaust methods.

2.1.2.a Continuous Dyeing

The primary source of BOD from continuous dyeing is the soap-off chemicals (surfactants) and the dyeing auxiliaries used in the pad bath, which may wash off. Also, reducing agents sometimes give high BOD values. Because of the continuous nature of these processes, the waste streams are easily segregated for heat recovery and other management strategies. Since the waste from continuous dyeing is usually mainly wash water, the chemical content is usually relatively low compared to desizing or scouring wastes or spent batch dye liquors. Thus, BOD source reduction in continuous dyeing processes does not hold the potential for improvements that batch dyeing does.

2.1.2.b Batch Dyeing

Problems with spent dye liquors from batch dyeing are much more difficult to handle because:

1) waste streams are usually dumped into common pits or trenches, making segregation difficult,

2) batch waste dumps occur at discrete intervals, timing is not predictable, and any restrictions on timing cause severe scheduling problems, and

3) the nature of the processes and chemicals used vary greatly.

There has been interest in dye waste reuse; however, only a few direct reuse situations have been commercially adapted. One of these is dyebath reuse, which is discussed in detail in Section 4.1.4 of this document.

Another example of reuse of dyehouse batch processing waste is the reuse of final rinse/softener baths (especially for hosiery) for prescouring the next batch of substrate, especially synthetics. Presumably, after softener is exhausted onto the substrate, its emulsifier system is still available for scouring fiber finish and knitting oils from the next hatch. Energy savings also occur because the exhausted softener bath is usually hot.

The BOD values of some dyeing assistants are given in Table 2.1.2.b-I. On a class-by-class basis, the types and amounts of dyeing assistants used vary greatly. Table 2.1.2.h-II summarizes waste characteristics (BOD) for each class of dye that is commonly applied by exhaust methods. For a discussion of machines, see Water Conservation (Section 3.3.1).

2.1.3 Finishing

Finishing is typically a continuous process that produces little or no waste water except perhaps noncontact cooling water and some afterwashing

Table 2.1.2.b-I

BOD Values for Dyebath Auxiliaries* [14, 15]

Product	5-day BOD (ppm)
Anthomine (wool dyeing)	90,000
Carbopen (penetrant)	20,000
Dyes (various)	0 to 100,000
Dyes (Sulfur)	about 100,000
Dyes (disperse)	about 30,000
Dyes (direct)	about 80,000
Dyes (azoic)	about 20,000
Azoic couplers (B-naphthol)	100,000
Formopon (hydra/formaldehyde strip)	270,000
Gluconic acid & lactone (vat)	520,000
Glucose corn syrup (vat)	530,000
Lanazin tip (albumin derivative)	90,000
Fluorescent brightener (leucophor)	330,000
Metachloron (fix)	0
Peregal OK	20,000
Rexan 0 (EO leveler)	20,000
Sodium acetate (buffer)	320,000
Sulfoxite (strip)	270,000

*Extensive private lists of BOD data for dyebath auxiliaries are circulated.

Table 2.1.2.b-II

BODs of Dyeing Assistants (ppm)

Class	Fiber	Machines	Chemicals	Bod contribution to waste
Acid	Wool Nylon	Stock Skein Package Jig Beck Jet Beam	Surfactant Leveler Retarder Acid Dye Lubricant Salt	Moderate (varies) Varies (may exhaust) Varies Low LOW Varies (may exhaust) Nil
Basic	Acrylic Other polymers	Stock Package Beck Jet Beam	Surfactant Leveler Retarder Acid Dye Lubriant Salt Carrier	Moderate (varies) Varies (may exhaust) Varies Low LOW Varies (may exhaust) Nil Varies (may be high)
Direct	Cellulose	Stock Package Jet Beck	Alkali (weak) Surfactant Retarder/ leveler Salt Lubricant Fixative Dye	Nil Varies (moderate) Varies (moderate) Nil Varies (may exhaust) Low (exhausts) Low
Disperse	Synthetic	Stock Package Beck Jet Beam	Acid (weak) Dispersant Dye Carrier Lubricant Reductive/ afterscour	Low High High (dispersant) High (varies) Varies (may exhaust) Moderate to high
Fiber Reactive	Cellulose (wool)	stock Jig Jet Beam Beck Skein	Alkali (strong) Salt Dye Dye Lubricant Soap-off	Nil Nil Nil Nil Varies (may exhaust) Moderate (varies)
Naphthol Sulfur } Vat	Cellulose	Any . . . (total production amount by exhaust is relatively low in NC)	Reducers, oxidors Dye Lubricant Buffer	}Varies greatly

waste (rarely). Occasionally there is condensate from steam heated equipment also, but the quantity is quite small compared to dye and preparation waste. Another source of potentially significant waste is dumping of unused finish mixes containing resins, catalysts, wetters, softeners, builders, and other materials. A list of BODs by common finish components is shown in Table 2.1.3-I [14,15]. Source reductions for finishing can be accomplished by adding and reusing finish mixes rather than dumping whenever possible.

A few types of finishes are applied by exhaust methods. These are generally done after, or as part of, the dyeing process and include softeners, lubricants, fixatives, and other special finishes (flame retardants, soil release, anti-bacterial, etc.).

In general, wastes from these are difficult to control, and continuous processes should be used if possible to avoid waste water loads associated with these chemicals. Sometimes these wastes can be reused (see Section 4.1.3).

2.1.4 Other Chemicals

Table 2.1.4-I gives BODs of some chemicals typically used in Wet processing which have not been in the tables previously presented in this document [14,15]. In addition to this list of miscellaneous processing chemicals, it is important to consider nonprocess chemicals such as:

- . machine cleaners
- . shop chemicals
- . biocides
- . insecticides
- . boiler treatment chemicals

Table 2.1.3-I

BODs of Finishing Chemicals* [14,15]

Aerotex Resin M-3 (melamine)	230,000
Aerotex Softener H	30,000
Aerotex Syrup 250 conc. (UF)	50,000
Ahcovel G (carbamate)	20,000
Amioca (finishing starch and wax)	70,000
Avitex SF (softener)	350,000
Avitone A (softener)	0 to 30,000
Casein	250,000
Catalyst AC	20,000
Cetosol SF (resin)	240,000
Concental #60 (softener)	1,000,000
Crystal gum (finishing starch)	90,000
Dextrin (finishing starch)	500,000
Dimethylol urea	100,000
Finish TS (soybean oil)	390,000
Formaldehyde, 37%	370,000
Lustramine (softener)	330,000
Lustrasol (softener)	200,000
Meleine RS (anti-fading agent)	300,000
Methacrol FNH (resin)	40,000
Nopco 1656 (spinning)	120,000
Proxol T (carding)	200,000
Resloom HP Special (MF resin)	100,000 to 140,000
Resloom M-75G (MF resin)	140,000
Rhonite 313 (UF resin)	110,000
Rhonite 610 (UF resin)	50,000
Rhonite R-7 (UF resin)	70,000
Rhozyme LA (enzyme)	20,000
Softener Cream 25% (tallow)	390,000
Solvool (softener)	640,000
Urea	90,000
Vel (sulf. glyceride cocamide)	270,000
Wool Finish B	570,000
Zelan AP paste (water repellent)	190,000
Zeset S (resin)	70,000

*Extensive private lists of BOD data for finish chemicals are circulated.

Table 2.1.4-I

BODs of Other Processing Chemicals [14,15]

Acetic acid 56%	300,000 to 360,000
Acetic acid 80%	520,000
Acetic acid 84%	620,000
Acetone	1,220,000
Allyl alcohol	20,000
Analine oil	1,500,000
Butyl acetate	520,000
Diastafor L (enzyme)	20,000
Diethylene glycol	20,000 to 60,000
Dypenolsed (mercerizing assistant)	390,000
Ethanol	930,000
Ethyl acetate	660,000
Ethylene glycol	160,000
Mineral spirits (Extender 31)	80,000
Formaldehyde 37%	370,000
Formic acid	20,000
Glycerine 88%	640,000
EDTA (Inhibitor M)	10,000
Isopropyl acetate	260,000
Methanol	800,000
Methyl isobutyl ketone	120,000
Monochloro benzene	200,000
Morpholine ($O = CH_2 - CH_2 = NH$)	30,000
Oxalic acid	140,000
Rapidase M (enzyme)	40,000
Red oil (sulfi castor oil)	680,000
Serizyme (enzyme)	20,000
Soaps	550,000 to 1,550,000
Sodium acetate	320,000
Sodium hydrosulfite (hydro)	220,000
Sodium sulfide (sulfur dyes)	220,000
Syton W-20 (silica)	0
Sulfonated castor oil	680,000
Tallow soap	55,000
Tallow	152,000
Triethanolamine	0 to 10,000
Urea	90,000
Glucose	710,000
Gelatin	910,000
Caustic	0
Soda ash	0
Ammonia	0
Potassium carbonate	0
TSP	0
Perborate	0
Silicate	0
Peroxide	0
Salt	0
GL salt	0
Sulfuric acid	0
Hydrochloric acid	0

If any of the above enter a waste stream, substantial pollution loads are likely to result. Furthermore, these chemicals are usually not as well controlled as process chemicals in a typical textile operation.

2.2 Toxicity

One of the primary environmental concerns now under study is discharge of toxic materials from point sources. Acute bioassay toxicity tests on textile mill effluents have shown varying degrees of aquatic toxicity [9,17,18,19]. Many mills' treated wastes show low toxicity in several tests, while others have shown high aquatic toxicity even in relatively low concentrations.

The exact identity of these toxics is not known nor is the identity of precursors of water borne toxics in textile processing. This subject is currently under study. In spite of the lack of specific information, studies of textile wastes and knowledge of the nature of textile chemicals, dyes, and processes allows for certain generalities.

Types of materials that may be expected to predominate in toxic textile waste waters include [11]

- . metals
- . nondegradable surfactants
- . toxic organic materials such as phenols, aromatic solvents
methylene, chloride, perchloroethylene, and oxalic acid, to
name a few.

2.2.1 Metals

Data published by the American Dyestuff Manufacturers Institute [20] show that metals can be expected to be present in varying amounts in different dye classes. This is shown in Table 2.2-I. Of course, individual members of each dye class vary widely in metal content.

Case History

A survey of dyes, performed in the mid 1970s, showed that the primary source of copper in wet processing waste from a major North Carolina mill was from dyestuffs. A check of each of the dyestuff showed that approximately 95% of the copper in the effluent originated from 13 dyestuffs which were manufactured with high copper contents:

Name	Percentage Cu 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 Resinfast Blue 2R	2.50
Sirius Supra Turquoise LG	2.29
Superlitefast Blue 2GLL	1.00
Direct Navy OFS	0.70
Belamaine Red 3BL	4.00
Solophenyl Brown BRL	3.00
Fastolite Blue L	2.70
Atlantic Black NR	1.50

Each of these dyes contained copper as an integral part of the molecular structure or its chromophore; therefore, most of the metal will exhaust onto the fabric with the dye. However, direct dyes typically remain 5% to 15% unexhausted in spent dye liquors. Thus some metal is discharged as waste. This particular mill did not use vat or fiber reactive classes for exhaust dyeing. Other metal sources that were specifically identified in this mill and which are typically present in wet processing operations were:

Table 2.2-I

Average Metal Content of Selected Dyes (ppm) [20]

Metal	Dye class					
	Acid	Basic	Direct	Disperse	Fiber reactive	Vat
Arsenic	< 1	< 1	< 1	< 1	1.4	< 1
Cadmium	< 1	< 1	< 1	< 1	< 1	< 1
Chromium	9	2.5	3.0	3.0	24	83
Cobalt	3.2	< 1	< 1	< 1	< 1	< 1
Copper	79	33	35	45	71	110
Lead	37	6	28	37	52	6
Mercury	< 1	0.5	0.5	< 1	0.5	1.0
Zinc	< 13	32	8	3	4	4

- .Oxidizers for vat and sulfur dyes (chromium)
- .Copper sulfate aftertreatment for direct dyes
- 9 Metal catalyst used for curing resins (zinc, aluminum)
- .Flame retardant, soil release, and water repellent finishes
- .Greige goods
- .Dye stripping agents such as permanganate, zinc sulfoxylate-formaldehyde, and dichromate

Two of these (oxidizers and aftertreatments) are directly related to dye application and are sometimes used to insure complete fixation and/or entrapment of the dye within the fiber. An example of this is the use of copper sulfate to aftertreat direct dyes, rarely practiced now in favor of the use of organic resinous fixatives. These resinous fixatives have higher nitrogen content and BOD, but have no copper content. An alternative procedure that avoids heavy metals and BOD both is to use epsom salts as an antimigrant until the fixative can be applied from a continuous resin finish formulation.

Also, certain dye classes require oxidation and/or reduction during the application and fixing of the dye. These dyes (particularly vats and sulfurs) were formerly oxidized with dichromate, but are now almost universally oxidized with other materials such as iodate, bromate, peroxide, etc.

Finally, repair procedures for many classes of dye can involve the use of metals and/or other toxic materials. One type is the zinc sulfoxylate-formaldehyde type of dye stripping agent used on some classes of dyes. This type of repair procedure can contribute to zinc content of waste streams. Another common type of stripping procedure for resin finishes is oxalic acid. This material is known to be toxic. A stripping procedure involving phosphoric acid and urea is equally effective for most resin finishes and with

much lower toxicity. These stripping procedures are for repair of defective fabric, but one source of toxic stripping agents that is sometimes overlooked is the machine cleaners used for dyeing machines, pad rolls, etc. These processes frequently are not controlled to the same extent as the dyeing processes, and the machine cleaner specialty chemicals frequently contain toxic solvents.

Another source of toxics that sometimes is overlooked is maintenance chemicals. The typical textile mill usually has some sort of approval procedure and quality control for raw materials used in processing (see Section 3.4), but sometimes maintenance chemicals escape approval because they do not directly affect the mill's direct cost and quality control, and because they are purchased and used less frequently than process chemicals. The control and evaluation of these materials should not be overlooked. Typical contents include methylene chloride, perchloroethylene, and other highly toxic materials.

Other types of nonprocess chemicals that have been known to contribute to toxicity of waste waters include biocides and herbicides. Biocides are frequently used in cooling-towers and nonprocess water purification and processing. Biocides also are used in certain applications such as finishes for hosiery, tents, awnings and tarpaulins. Herbicides are used to control grass, weeds and other vegetation near bulk storage tanks, such as areas within a spill control berm, especially tanks of flammable materials such as natural gas, LP gas, fuel oil, and varsol.

2.2.2 Surfactants

Another group of materials that frequently contributes to textile mills' aquatic toxicity problems includes surfactants, detergents, emulsifiers, and

dispersants [21]. These are universally used in textile wet processing. The EPA development document for textile effluent guidelines clearly states [22] substitution must be made carefully to avoid introducing nondegradable detergents (which will contribute to aquatic toxicity) for the purpose of lowering ROD. This advice has been frequently ignored in practice, primarily because surfactants are usually proprietary mixtures and the degradability data are not known to the mill.

2.2.3 Other Toxics

More subtle problems can arise in relationship to the potentially dangerous degradation products of textile (and other) dyes [23]. An example of such a dye is food red #5 which is known to degrade to products that are carcinogenic and mutagenic (Fig. 2.2.3-1). In this case, the dye itself is not harmful, but the degradation products that might occur during metabolism (or in the case of a textile dye, reductive stripping or other degradation) are suspect.

In other cases, for example food red #1 (FD&C Red 41, neither the dye nor its degradation products are suspect (see Fig. 2.2.3-2).

A class-by-class and/or dye-by-dye evaluation can be made for textile dyestuffs. Such an analysis has not been published; however, one could generally expect that the degradation products from dyes of certain types might be suspect. Figure 2.2.3-3 shows chemical analogs that might be substituted in dye synthesis to give safer dyes, in terms of other reductive degradation products.

One common type of procedure used in essentially all commercial dyeing operations is "stripping", or removal of colorants from textile substrates for repair purposes. There are many procedures that can be used for this purpose,

CARCINOGENIC AZO DYE

ACID RED 26 (16150) (FORMERLY FOOD RED 5)

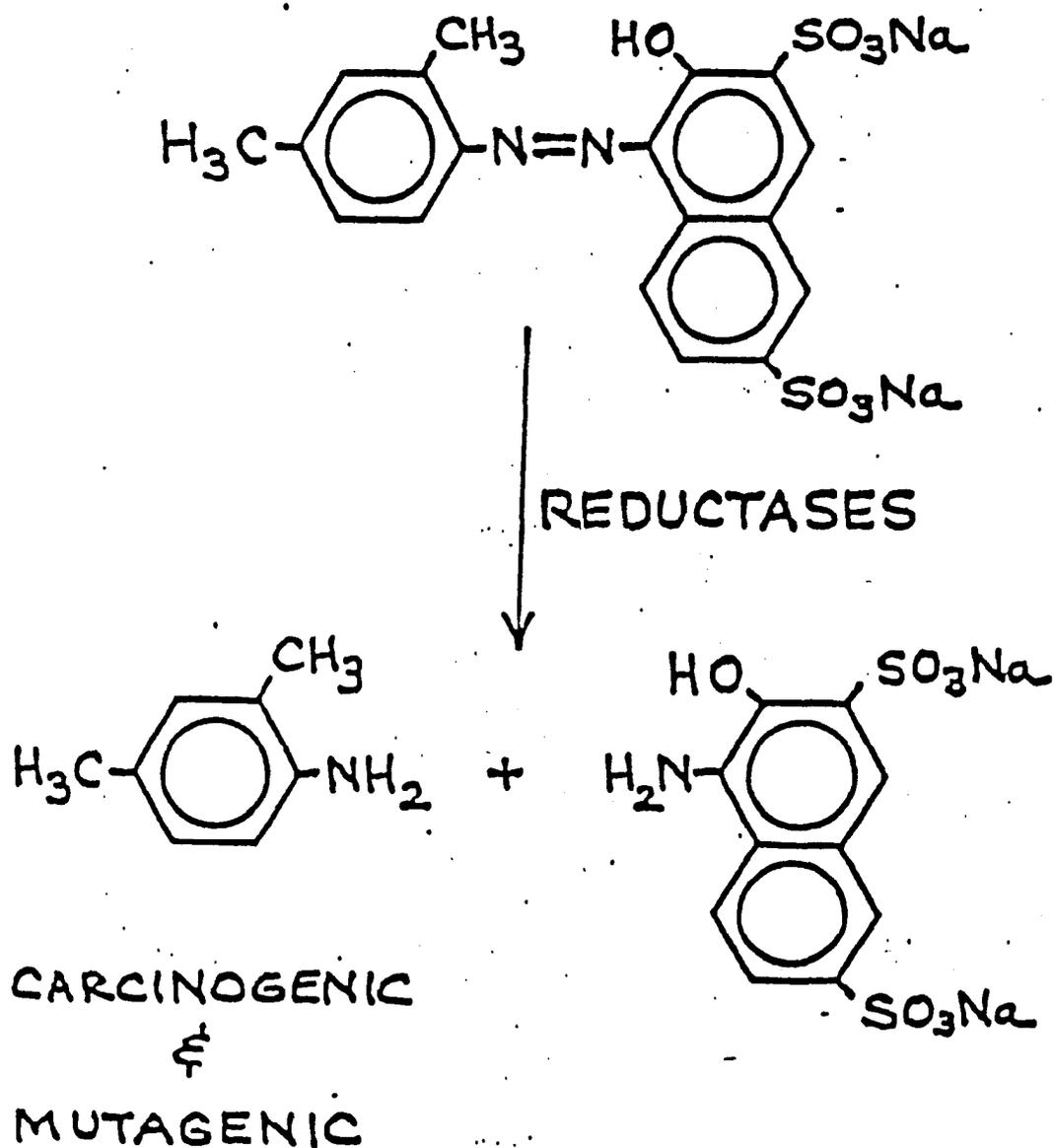


Figure 2.2.3 - 1 Carcinogenic Azo Dye

NON-CARCINOGENIC AZO DYE

FOOD RED 1 (14700) (FD&C RED NO. 4)

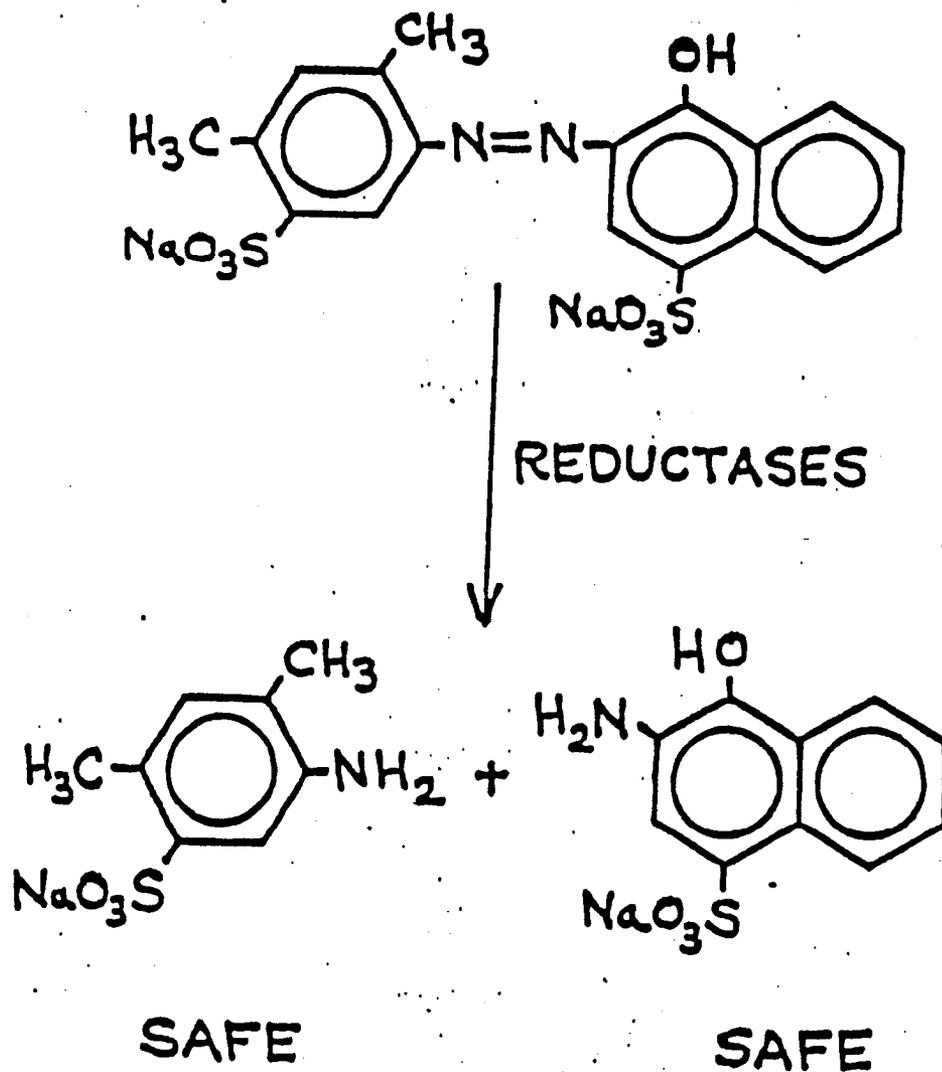
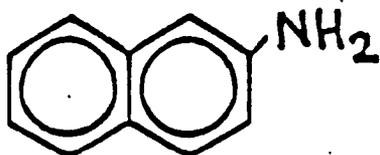
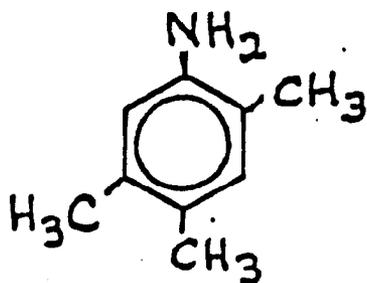
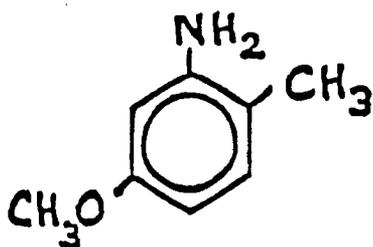
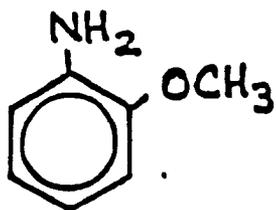


Figure 2:2.3 - 2 Non Carcinogenic Azo Dye

HOPE FOR THE FUTURE

3

MUTAGENIC



NON-MUTAGENIC

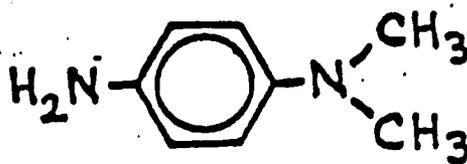
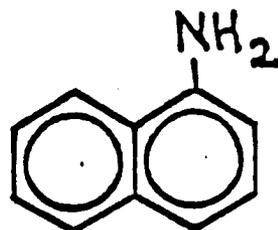
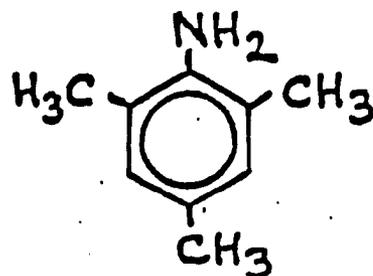
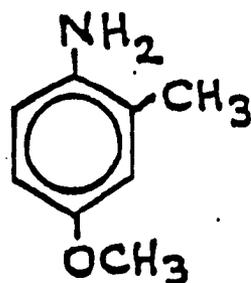
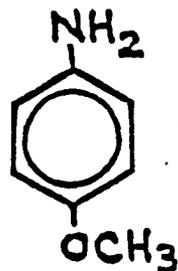


Figure 2.2.3 - 3 Alternative Intermediates

HOPE FOR THE FUTURE

37

MUTAGENIC

NON-MUTAGENIC

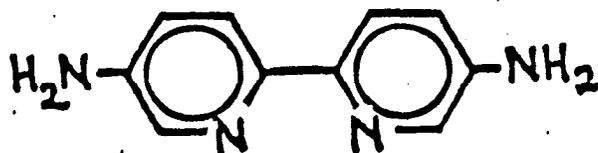
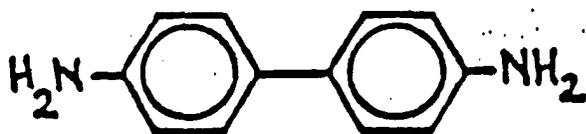
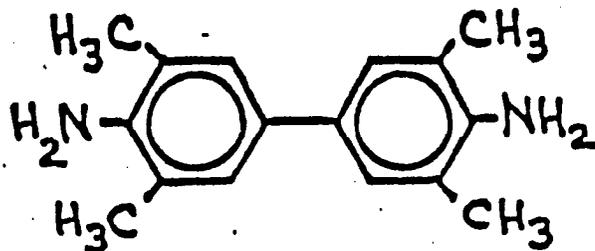
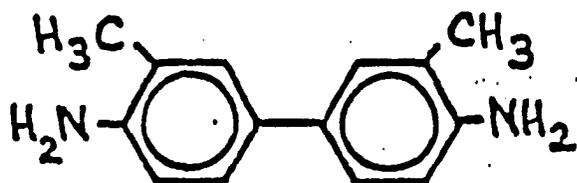
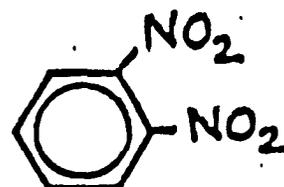
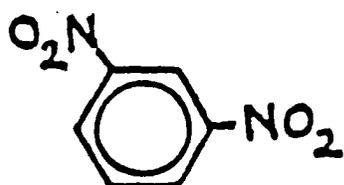
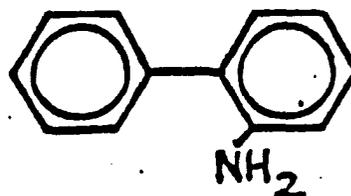
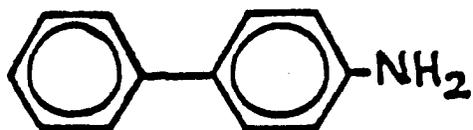


Figure 2.2.3 - 3 Alternative Intermediates (Cont)

and each one has its own unique features. Some important points of variation are:

- .1) finish removal (liberates formaldehyde)
- .2) pH (acid or alkaline)
- .3) oxidation or reduction bath
- .4) type of oxidizer/reducer
 - chromium based (Dichormate)
 - zinc based (Parolite/Discolite)
 - chlorine containing (Chlorite, Hypochlorite)
 - peroxy types (Peroxide, Perborate)
 - manganese based (Permanganate)
- .5) use of aromatic solvents and/or surfactants as stripping assistants, such as phenolic materials, biphenyl, orthodichlorobenzene, etc. These may become polychlorinated to form toxic materials or degraded to produce lower molecular weight phenolic materials.

For stripping to be successful, colorants must be degraded to water soluble products and/or rendered colorless. This means, in most cases, that the chromophore part of a dye molecule must be degraded into products that, in most cases, are similar to the dye intermediates from which the colorant was synthesized. Some of these are hazardous materials, and stripping waste containing these are discharged to the effluent stream. Naturally, the specific type of stripping procedure and original colorant selection will determine the products that will be in the effluent.

Futhermore, all batch dyeing operations discharge spent dye liquors containing typically 5% to 15% of the total amount of dyestuff that was used.

This occurs because batch dyeing is an equilibrium process and therefore some residual dye will always be left in spent dye liquors. These could also be degraded in waste treatment systems to the same kind of products that are produced by stripping.

2.3 Alkalinity/Acidity; pH

An analysis (similar to the previous discussion of BOD or toxics) can be made for pH contributors. Typical textile mills have several sources of acids and alkalis. One particular mill had the following overall acid and alkali use:

Common Acids and Alkalis and the Use of Each

Name of chemical	Pounds used per week				Total # (four weeks)
	1	2	3	4	
Acetic acid	4500	3600	4500	3600	16200
Alkaflow	6363	7322	6370	7260	27520
Ammonia	0	0	0	0	0
Bicarbonate	0	0	0	0	0
Caustic (50%)	2460	2530	2530	3795	10815
Formic Acid	0	0	0	0	0
MSP	0	0	0	0	0
Muriatic Acid	0	0	0	0	0
Soda Ash	1700	900	600	1300	4500
Sulfuric Acid	1096	369	728	661	2854
TSP	900	1000	1800	2100	5800
TSPP	0	0	65	0	65
Water (M gal)	6.72	8.00	7.89	7.85	32.46

Use of these quantities of acids and alkali in this amount of water would give an overall pH around 10.7. Of course, this would fluctuate between wide limits as different processes were run. Typical data for 24-hour tests of pH are shown for two mills in Figures 2.3-1 and 2.3-2.

The control of effluent pH can be a difficult problem to handle from a process point of view because in many cases there is simply no substitute for the use of alkali or acid. This means that reuse, recovery, recycle or

Hourly Variation of pH in Textile Raw Waste

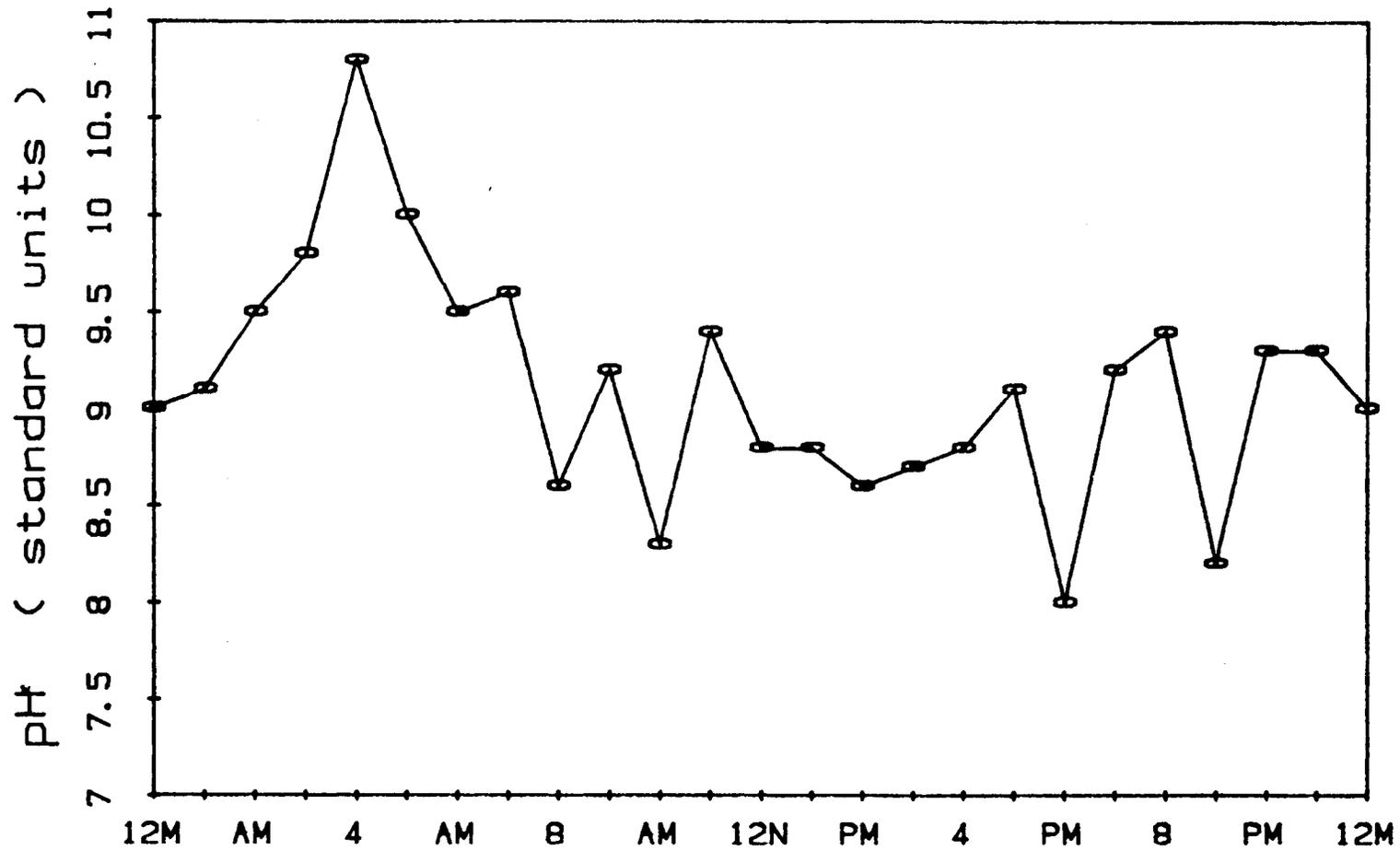


Figure 2.3 - 1 [24]

pretreatment (equalization and/or neutralization) are sometimes the only alternatives.

Reuse/recycle potential does exist in certain waste streams, and these are discussed in a general way in the following paragraphs. Of course, the details of any such system will be very product- and site-specific.

Preparation processes include several steps. Desizing of starch sized fabrics contributes little or nothing to alkalinity/acidity of waste streams. Other sizes, such as CMC, PVAc, PVOH, and PAA are typically removed in alkaline solutions. The contribution of these desizing processes can be a significant portion of total alkalinity. Since the desizing process is usually done continuously, waste streams can easily be neutralized by the addition of acid as produced. Source reduction would involve minimizing the amount of alkali used; usually, little is needed.

Scouring and bleaching of synthetics should be done using minimal amounts of alkali, but scouring of cotton requires large amounts of alkali. When cotton scouring and/or bleaching is done in a continuous process unit, there is potential for neutralizing or reuse of waste streams as described in Section 4.1.2. Typical concentrations of alkali for cotton scouring are 2% to 4% of caustic (50%) based on the weight of the fabric processed.

Perhaps the greatest potential source of alkali in preparation is the process of mercerization of cotton. This uses caustic concentrations of about 20%. Wherever a significant amount of fabric is mercerized, the potential for caustic recovery as a source reduction strategy should be considered (see Section 4.1.3).

Dyeing processes vary in acidity/alkalinity depending on the substrate and dye class. General practice for the exhaust dyeing of various classes is:

- . Acid for nylon and wool - exhaust from weakly to strongly dyebaths (pH 3 to 7), usually using formic acid, acetic acid, or a buffer salt for pH control.
- . Basic for acrylic and copolymers - exhaust from weakly acid dyebaths (pH 4 to 5), usually using acetic acid for pH control.
- Direct for cellulose - exhaust from weakly alkaline baths (pH about 8), usually using soda ash for pH control.
- . Fiber reactive for cellulose - exhaust from neutral baths with massive amounts of salt, then cause reaction to occur by adding large amounts of alkali such as caustic, soda ash, silicate and/or TSP. The pH will typically be above 10.
- . Naphthol for cellulosic - prepare a diazo salt in a strongly acid (pH < 3) bath, then react with a (beta)-naphthol coupling agent. Effluent is very acidic. This applies also to other diazotized and developed colors.
- . Vat and sulfurs for cellulose - typically exhausted in such a way that the effluent is alkaline, then oxidized.
- . Disperse for synthetics - exhausted from weakly acid (pH 4.5 to 6) solutions.
- . Practices for dyeing blends vary from the above.

Stripping and machine cleaning procedures (as discussed in Section 2.2) can produce extreme pH variations.

One of the most difficult problems facing textile dischargers can be meeting typical POTW regulations of 6 to 9 pH limitations. Possible strategies include reuse of continuous streams, recovery systems for caustic (mercerization), and minimizing amounts of alkali used in varying processes.

However, a typical mill that scours, bleaches, dyes and finishes cotton and blends has little or no chance of staying in the 6 to 9 range. Typical average values are above 11. This means that some pretreatment is necessary and that equalization alone will generally not be enough.

2.4 Air Emissions

Although the primary emphasis in this document is water-borne waste streams, air emissions will be discussed here briefly. Air emissions emanate from several places in typical textile operations:

- hot air dryers
- dyeing machines
- storage tanks
- warehouse area
- fugitive (general ventilation)

One important waste product from finishing is air emissions from high temperature drying and curing ovens. Typically these contain varying amounts of volatile components of the finish mix as well as any volatile residues left in fabric from prior processing. Proper preparation and judicious selection of preparation, dyeing and finishing agents can help reduce these. The primary emphasis in this area has been use of abatement equipment rather than source reduction. This can sometimes be combined with heat recovery from air exhaust to provide a return on investment.

Of course, a textile processor has no way of knowing with certainty whether or not chemicals are being emitted without testing each potential source. That would take many months--if not years--to do. It is not the intent of the Division of Environmental Management to require such testing at this time, but it is desirable for each facility which has an air permit to make estimates based on information in hand.

Such estimates can be made, keeping in mind knowledge and records of major production chemicals used in specific processing. The OSHA 20 form (MSDS) would be an adequate guide to the components of a formulated chemical specialty. A list of chemicals that are of particular interest is shown in Table 2.5-I. Therefore, one can compare the list to the OSHA 20 form for each chemical used, to determine the presence of the substances of concern, and to confirm the information given below, for mill-specific situations.

There are 80 materials on the list. There is no reason to expect 71 of them to be in textile operations.

Of the remaining nine, two are almost certainly present in essentially all textile operations:

Acetic acid	CAS# 64-19-7
Formaldehyde	CAS# 50-00-0

Acetic acid could be emitted from bulk storage tanks and, to a lesser extent, it is possible that it may be emitted from dyeing machines and/or driers. The emissions from bulk storage tanks would be through the vents and would occur during filling and due to breathing losses. There are methods which can be used to estimate these bulk-tank emissions. Calculations show that one could expect that any large acetic bulk storage acid tank will emit amounts of vapors that exceed the "trace" limits, if not equipped with abatement equipment. As to the driers and dyeing machines, one would expect that the emissions will be well below the trace amounts. This could be verified by testing.

Formaldehyde may be emitted from bulk resin storage tanks, finished fabric warehouses, driers, and curing ovens. Emissions from bulk storage tanks may be above the trace amount limits. As to the emissions from driers, this also may be expected to be above trace amounts. To dry and cure all

Table 2.5-I
Toxic Air Pollutants

Toxic air pollutant	Trace emission rate (lbs/hr)	Trace emission rate (lbs/15 min)	CAS#
1. Acetaldehyde	1.31	4.94	75-07-0
2. Acetic acid	0.18	0.67	64-19-7
3. Acrolein	0.001	0.01	107-02-8
4. Acrylonitrile	0.03		107-13-1
5. Aluminum and compounds	0.07		
6. Ammonia	0.13	0.49	7664-41-7
7. Aniline	0.07		62-53-3
8. Arsenic and compounds	0.0000002		
9. Asbestos	0.0004*		1332-21-4
10. Aziridine	0.007		151-56-4
11. Benzene	0.0002	1.37	71-43-2
12. Benzidine	0.000000005		92-87-5
13. Benzylchloride	0.03		100-44-7
14. Beryllium and compounds	0.00001		
15. bis-Chloromethyl ether	0.000004		542-88-1
16. Bromine	0.005	0.03	7726-95-6
17. 1,3-Butadiene	0.16		106-99-0
18. Cadmium and compounds	0.0003		
19. Carbon disulfide	0.21		75-15-0
20. Carbon tetrachloride	0.21		56-23-5
21. Chlorine	0.02	0.16	7782-50-5
22. Chlorobenzene	2.56		108-90-7
23. Chlorofluorocarbons	55.67	173.99	
24. Chloroform	0.36		67-66-3
25. Chloroprene	0.32		126-99-8
26. Chromium and compounds	0.0000001		
27. Cresol (all isomers)	0.16		1319-77-3
28. p-dichlorobenzene	3.29	12.36	106-46-7
29. Di(2-ethylhexyl)phthalate	0.03		117-81-7
30. Dimethyl sulfate	0.003		77-78-1
31. Dioxane	0.65		123-91-1
32. Dioxins	4.4 x 10 ⁻¹¹		1746-01-6
33. Epichlorohydrin	0.07		106-89-8
34. Ethylacetate	10.25		141-78-6
35. Ethylenediamine	0.18		107-15-3
36. Ethylene dibromide	0.0002		106-93-4
37. Ethylene dichloride	0.29		107-06-2
38. Ethylene glycol monoethyl ether	0.13		110-80-5
39. Ethylene oxide	0.01		75-21-8

*For asbestos, assume 30 fibers greater than 5 microns in length are equivalent to a weight of one nanogram.

Table 2.5-I (continued)

Toxic Air Pollutant	Trace emission rate (lbs/hr)	Trace emission rate (lbs/15 min)	CAS#
40. Ethyl mercaptan	0.007		75-08-1
41. Fluorides	0.01		
42. Formaldehyde	0.01	0.05	50-00-0
43. Hexachlorocyclopentadiene	0.0007		77-47-4
44. Hexane	1.31		110-54-3
45. Hydrazine	0.0007		302-01-2
46. Hydrochloric acid	0.051		7647-01-0
47. Hydrofluoric acid	0.01	0.09	7664-39-3
48. Hydrogen cyanide	0.08		74-90-8
49. Hydrogen sulfide	0.10	0.38	7783-06-4
50. Iron pentacarbonyl	0.005	0.02	13463-40-6
51. Lithium and compounds	0.0001		
52. Maleic anhydride	0.007		108-31-6
53. Manganese and compounds	0.007	0.05	
54. Mercury and compounds	0.00007		
55. Methyl chloroform	13.91		71-55-6
56. Methylene chloride	2.56		75-09-2
57. Methyl ethyl ketone	4.32	16.20	78-93-3
58. Methyl isobutyl ketone	1.50	5.49	108-10-1
59. Methyl mercaptan	0.007		74-93-1
60. Nickel and compounds	0.000004		
61. Nitric acid	0.03	0.18	7697-37-2
62. Nitrobenzene	0.03		98-95-3
63. N-nitrosodimethylamine	0.00000004		62-75-9
64. Pentachlorophenol	0.003		87-86-5
65. Perchloroethylene	2.45	24.54	127-18-4
66. Phenol	0.13	0.69	108-95-2
67. Phosgene	0.002		75-44-5
68. Phosphine	0.002	0.01	7803-51-2
69. Polychlorinated biphenyls	0.003	0.01	1336-36-3
70. Polycyclic organic matter	0.0000007		
71. Styrene	1.57	7.78	100-42-5
72. Sulfuric acid	0.007		7664-93-9
73. Tetrachloroethane	0.05		79-93-9
74. Tetrahydrofuran	4.32	13.46	109-99-9
75. Toluene	2.74	10.255	108-88-3
76. Toluene diisocyanate	0.0002	0.002	26471-62-5
77. Trichloroethylene	1.97	19.78	79-01-6
78. Vinyl chloride	0.0005		75-01-4
79. Vinylidene chloride	0.14	1.46	75-35-4
80. Xylene (all isomers)	3.18	11.99	1330-20-7

resin treated fabric on one oven will limit a processor to only one source. If several ovens are used and each emits formaldehyde above the trace amounts, each must be analyzed as a separate source. To be absolutely sure of the emission levels, testing could be done. It is not possible, in general, to estimate how much formaldehyde would be released in curing or warehouse storage, however, it may be significant.

There are seven additional chemicals on the list which may or may not be present in specific textile operations:

Chemical	CAS#	Potential source
Chlorine	7782-50-5	Shop, water treatment
Ethylene oxide	75-21-8	Drier stacks (wetting agents)
Hydrochloric acid	7647-01-0	Drier stacks (catalyst)
Methylene chloride	75-09-0	Shop, paint stripper, etc.
Perchloroethylene	127-18-4	Drycleaner, scour, carrier
Toluene	108-88-3	Becks, driers (carrier/scour)
Xylene	1330-20-7	Becks, driers (carrier/scour)
Ammonia	7664-41-7	Shop, storage tank
Tetrachloroethane	79-34-5	Shop, inspection (spot remover)
Trichloroethylene	79-01-4	Shop, inspection (spot remover)

A manufacturer should check each OSHA 20 for each type of chemical indicated (degreasers, spot removers, dry cleaning fluid, carriers, scours, etc.) to see if any of the above listed materials are present. Mass balance calculations will then indicate whether it exceeds the trace amount limits. A reasonable strategy to approach these problems is:

- (1) Review OSHA 20 forms for all chemicals to determine if any of the listed chemicals appear as components of formulated chemical specialties. Pay close attention to chemicals that are used in bulk as well as shop chemicals, solvents, degreasers, machine cleaners, etc.

- (2) If any do appear, try to estimate the rate of release to the air by mass balance (amount consumed per unit time in an operation).
- (3) If any estimates exceed the "trace" amount limits, then test for those specific items at the specific potential source with Drager tubes to determine if trace limits are exceeded. This is because the calculations are rough at best, and they may significantly overestimate emissions. The Drager test is inexpensive, direct, and quick.

3.0 WASTE REDUCTION STRATEGIES

There are several source reduction strategies that have successfully been used, including

- . Process Modification
- . Use of Alternative Methods
- . Chemical and Water Conservation
- . Chemical Screening and Substitution

These are discussed for some specific situations in Section 3.1 through Section 3.4.

3.1 Reduction by Process Modification

Several methods are available to the manufacturer to reduce these pollutants from waste streams. They include:

1. Reduction of chemical use
2. Chemical substitution
3. Recycle/renovation of batch treatment baths
4. Waste stream reuse
5. Recovery of chemicals from waste streams
6. Use of alternative processes
7. Treatment of waste streams (separate and/or composite)
 - equalization
 - neutralization
 - screening
 - etc.

In many cases, it is possible to reduce the amounts of chemicals used in textile processing without significant effect on product quality. Frequently

overused materials include defoamers, surfactants, lubricants and similar types of chemical specialties.

In the case of chemical substitutions to reduce waste loading, the situation is not well defined. Several problems complicate the situation including:

- Lack of BOD, toxicity, and other data from suppliers
- .Difficulties in correlating data on pure products to estimate effects in spent dye liquors and other waste streams
- .Difficulties in evaluating trade-off effects such as BOD vs toxicity (as discussed in Section 2.2)
- . Proprietary nature of chemical specialties

One way to evaluate the potential for oxygen demand/toxicity problems for a product or waste stream is to take into account both the COD and BOD of the material. These quantities are related in such a way that COD:BOD ratio is 2.5:1 to 5:1 for typical textile waste streams. Any waste stream that has very high (above 5:1) COD:BOD ratio indicates poor biodegradability of material. In many cases, BOD alone is not an adequate indicator of biodegradability. This subject has been studied [25] for many types of textile chemicals, including PVA, butyl benzoate, polyethylene, kerosene, and dyes such as direct blue 80, disperse red 68, disperse blue 139, and others.

In many cases, the overall waste situation is not improved by substitution. For example, the previously mentioned case or substitution of certain surfactants can result in lower BODs but increased toxicity of treated wastes. In other cases, materials exhaust from batch and become (temporarily or permanently) part of the product. They may be evolved later during drying or other high temperature processes as VOCs and/or PRs. Another example of trade-offs is the use of mineral vs organic acids/alkali which can substitute

•

BOD for acidity/alkalinity, which may help in specific cases. The use of epsom salts as an antimigrant can replace copper or organic resins as a dye fixative.

Finally, there are opportunities for overall reductions, including

- . Reduce chemical usage
- . Use synthetic sizes
- . Recovery
- . Stream reuse
- . Dyebath renovation/reuse
- . Process modification

The following sections (3.1.1 through 3.1.3) discuss each wet process in detail.

3.1.1 Preparation

Preparation processes, especially desizing and scouring, can be done on many types of equipment, both continuous and batch. The continuous processes have a somewhat greater potential for waste stream reuse since the waste stream is continuous, fairly constant in characteristics, and usually easy to segregate from other waste streams.

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

1. Recycle 3 - box or kier drain wastes to saturator
2. Use of countercurrent washing
3. Use of washer waste from scour operation for batch scouring

This is shown in Figure 3.1.1-1. Of course, preparation chemicals (including especially optical brighteners and tints) must be selected in such a way that reuse does not create quality problems such as spotting.

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

- .The streams occur intermittently.
- .The streams generally dump into pits and are not easily segregated.
- .The liquor ratios are much higher (typically 10:1 to 20:1) in batch preparation; therefore, the wastes are more dilute.
- .Preparation steps are frequently combined.

3.1.2 Dyeing

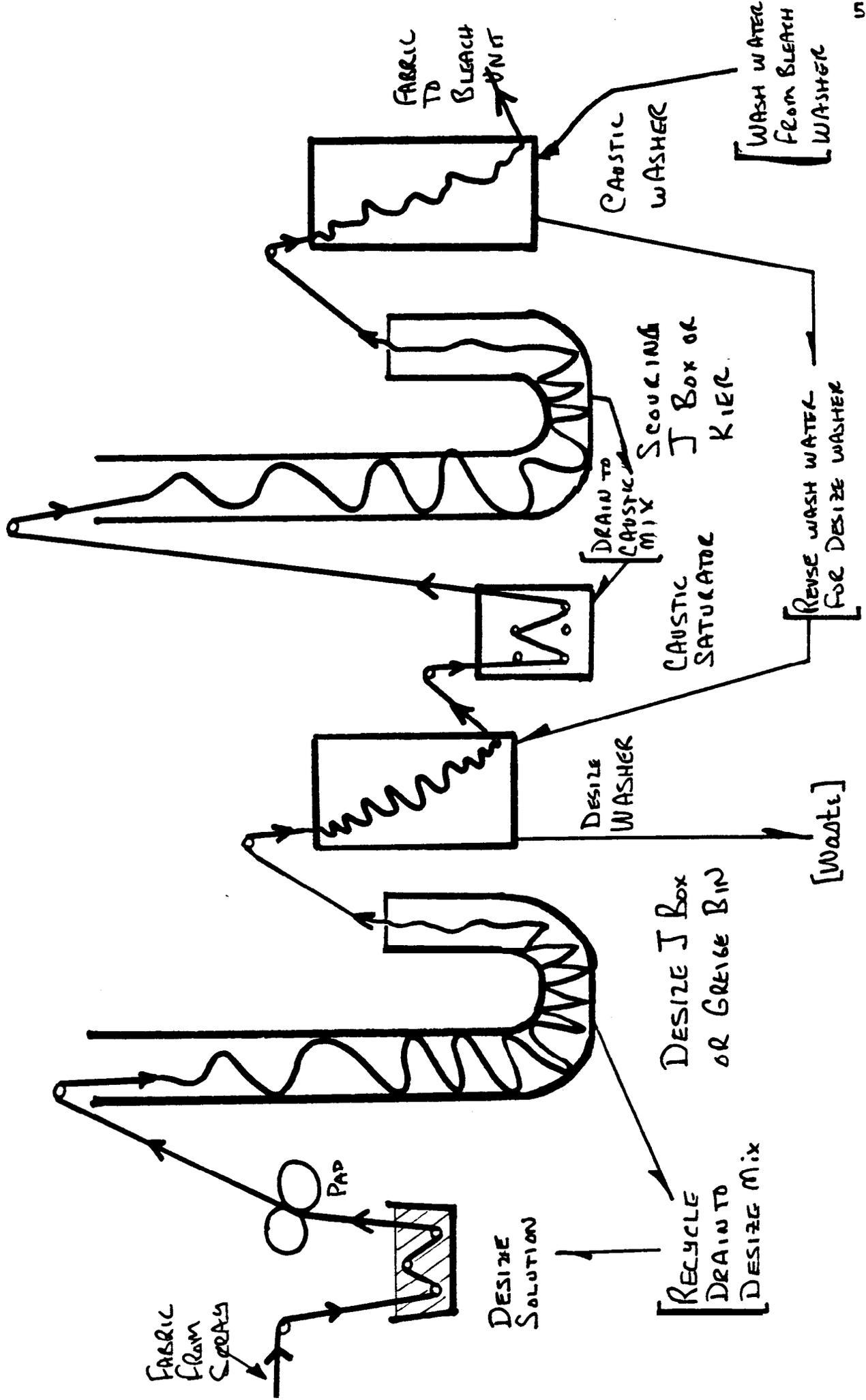
With dyeing processes, the following should be considered in making product substitutions.

Does the product, or portions of the product, exhaust? Many products such as dyes, dye carriers, softeners, lubricants, and retarders are blends. Some components may exhaust while others do not. For example, disperse dyes and colorants are commonly diluted with dispersants such as naphthalene sulfonic acid to make commercial dyes. The colorant will exhaust leaving the dispersant in solution, Thus, the BOD of the commercial dye is an indicator of the BOD load in the waste only to the extent that the dispersant contributes.

For dyes, this would vary. For softeners, lubricants, dye carriers and other emulsified products, the emulsifier system would be a major contributor, since it generally would not exhaust. The active materials (softener, carrier, etc.) would exhaust to various degrees. This means that the dyer

FIGURE 3.1.1-1

WASTE REUSE / RECYCLE IN CONTINUOUS PREPARATION UNIT



must examine not only the BOD of a product but also the BCD that is left in a residual dyebath after using a product.

The portions of a product (especially carrier) that exhaust will become part of the substrate, usually temporarily, until the substrate is dried at high temperature. Then these materials may become airborne waste (VOCs and PRs, typically). Examples of these materials are trichlorobenzene, dichlorobenzene, biphenyl, methyl naphthalene, orthophenyl phenol, and butyl benzoate.

Reduction strategies in this area would include:

- . Get as much information as possible from vendors, including OSHA form 20 and technical data.
- . Analyze spent dyebaths for residual materials.
- . Be aware of potential problem chemicals such as aryl phenol ethoxylates, branched alkyl phenol ethoxylates, chlorinated aromatics, and metals.

As pointed out above, the surfactant/dispersant/emulsifier content of products is a major contributor to BOD waste load because:

- (a) does not usually exhaust,
- (b) surfactants have relatively high BODs.

However, as in the case of scouring processes, lower BOD surfactants may not necessarily be desirable **since** they may contribute more to aquatic toxicity or treated wastes than the more degradable (higher BOD) surfactants.

Because of the widespread use of carrier materials (including "levelers") used for dyeing synthetic fibers with disperse dyes, and the high potential for contribution to waste loads, both water (BOD/COD/toxicity) and air (VOC/PR), careful consideration of carrier selection is necessary.

Table 3.1.2-I shows the BOD of some specific carrier-active materials.

Case History

One particularly interesting case history was reported recently [52]. A dyer was having problems with blotchy dyeings on jet dye machines. These problems were being caused by foaming of the dye bath due to excessive amounts of chemical specialties. To solve this problem a new "product" was substituted for all the other specialties already in the bath. This new "product" was nothing but water. This resulted in savings in cost, off-quality, and pollutant discharge.

3.1.3 Finishing

It is good practice to try to reuse the residual portions of finish mixes as much as possible by adding back to them the required components to make up the next mix. This is practiced commercially in many mills and saves both the pollutant load to the waste stream plus the cost of the materials saved (see Section 3.4). A simple technique to facilitate the dilution calculations is Pearson's Square [53].

Another strategy (for water conservation) is to return noncontact cooling water and steam condensates to either a hot water holding tank or a clear well. If neither of these is possible, segregate the waste streams from these sources which do not generally require treatment from other waste streams that do. This reduces hydraulic loads in treatment systems.

3.2 Pad Batch Dyeing

The pad batch (cold) method of dyeing cellulose is hardly a new concept [26-30]. It has been used quite successfully in a wide variety of applications. Benefits include essentially eliminating the need for salt or chemical specialties from the dyebath, with associated reduction in cost and

Table 3.1.2-I [5, 14, 15]

Material	BOD
Benzoates	1,250,000
Monochloro benzene	30,000
Orthophenyl phenol	6,000
Salicylates	24,000
Phenyl methyl carbitol	19,000
Phthalates	1,060,000
Xylene	0

pollution source reduction. In many ways, it is one of the most reliable and easiest-to-control methods available today for certain applications.

Strangely enough, however, it has not caught on in this country to the extent that it is used in Continental Europe or in England.

To quickly summarize the pad batch method, prepared fabric is impregnated with liquor containing premixed fiber reactive dyestuff and alkali; excess liquid is squeezed out on the mangle; the fabric is batched onto rolls or in boxes, and covered with plastic film to prevent absorption of CO₂ from air or evaporation of water, then stored for two to twelve hours (see Figure 3.2-1). The goods can be washed off in any of several conventional ways, depending on equipment available in the mill.

The method is interesting because it offers several significant advantages, primarily in its simplicity and speed. Production of between 75 and 150 yards a minute, depending on the construction and weight of the goods involved, is commonly reported. In fact, this kind of speed can make the limiting factor the wash-off facilities, which may not be able to keep up.

Another factor that has generated enthusiasm for pad batch is its flexibility, compared to a continuous range. Either wovens or knits can be done, and in many constructions. Frequent changes of shade are no problem because reactives remain water soluble, making cleanup easy. This fits many situations well, especially when versatility is required. The pad batch system can run the same cold dyeing fiber reactive combinations that are usually run on package dye, jigs, beams, becks, jets and other equipment. Washing-off can be done with becks, beams, continuous equipment or other available machines.

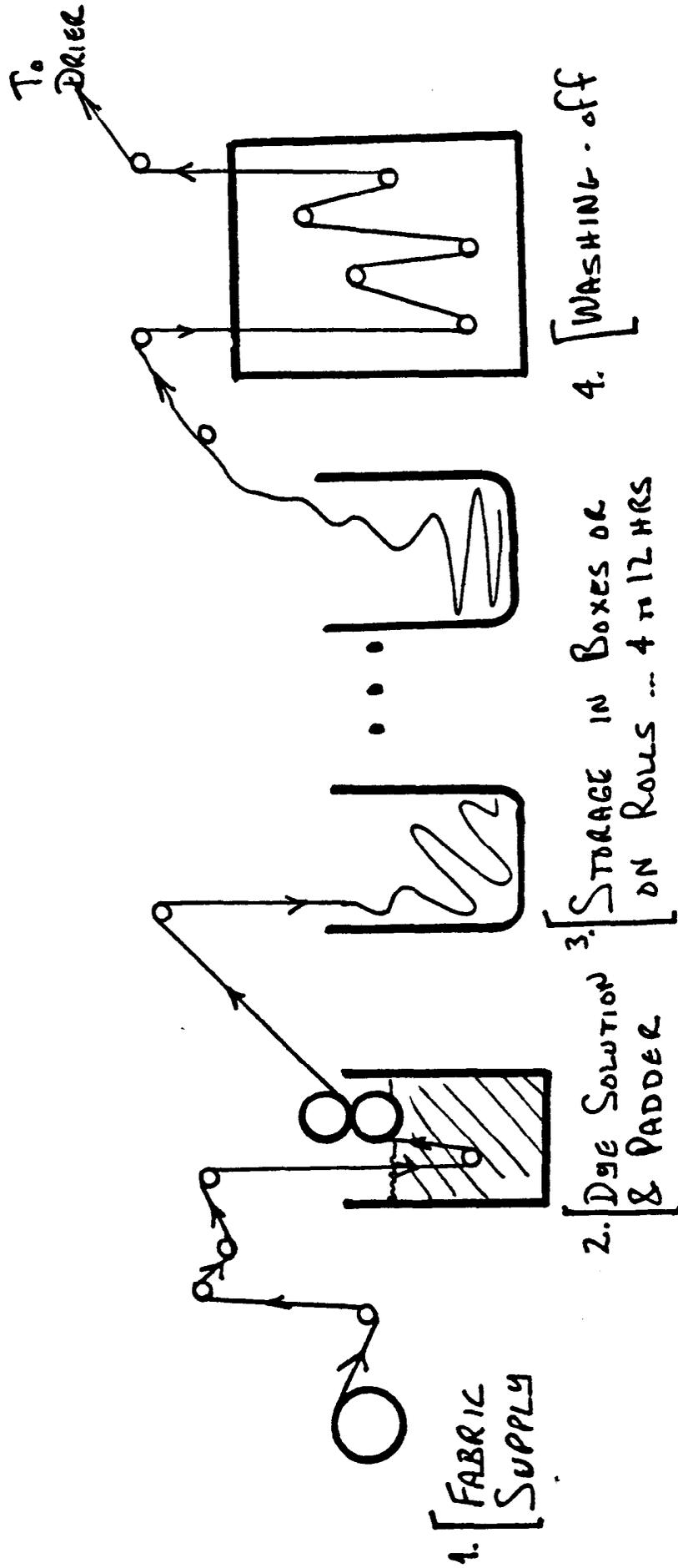


FIGURE 3.2 - 1 PAD/BATCH, STORAGE and WASH-off UNIT

Studies [30] have shown that pad batch dyeing for cotton, rayon and blends conserves energy, water, dyes and chemicals, labor and floor space. Water consumption for pad batch dyeing with beam wash-off is typically under two gallons per pound of dyed fabric, compared to typically 20 or more on atmospheric becks for the same fiber reactive dyed shades. Energy consumption is similarly reduced from about 9000 BTU's per pound of dyed fabric for becks to under 2000 BTU's per pound for pad batch with beam washing. Chemical use, and associated BOD and COD loadings for waste streams, can be reduced up to 80% compared to atmospheric becks. Labor costs are also reduced. For example, two workers per shift can dye 200,000 pounds of fabric per five-day week.

In general, the quality of pad batch dyeings is much better than other dyeing systems. Specifics of cost savings are shown in Tables 3.2-1, 3.2-11, and 3.2-III. Pad batch dyeings require highly reactive "cold dyeing" fiber reactive colors. Examples of brand names of such colors are:

Atlafix CX	(Atlantic)
Cibacron F	(Ciba Geigy)
Intracron C	(C&K)
Levafix E(A)	(Nobay)
Drimarine K	(Sandoz)
Procion M	(ICI)
Remazol	(Hoechst)

One key to successful use of the system by the dyer is pH control. While all respective dyes are not all equally sensitive, a pH of 10.5 to 11.5 will be ideal in most cases for 12 hour batching. An increase in pH may be necessary to increase reaction rate for short batch times (2 to 4 hours).

Table 3.2-I
 Comparison of Annual Operation Cost [30]

	Cold dyeing reactives on cotton pad/batch/2 beam wash-off stands	Conventional exhaust dyeing 100% cotton (19 becks)
Production (120 hr wk/ 50 wks/annum)	193,050 lbs/week or 9,652,500 lbs/annum	193,050 lbs/week or 9,652,500 lbs/annum
Labor costs	\$79,560	\$256,360
Fuel costs (Extra drying)	\$52,000 \$48,300	\$272,000
Water costs	\$ 8,700	\$ 98,500
Dye costs (Varies, see Table III)		
Chemical costs		
Salt	0	\$337,840
Alkali	\$19,112	\$ 82,820
	<u>\$207,672</u>	<u>\$1,047,520</u>

Table 3.2-11
Capital Investment [30]

Cost comparison of pad-batch with becks	
Pad batch dyeing system:	
Dye pad for knits	\$ 160,000
2 beam wash-off stands	
Installation estimated to be 30%	\$ 48,000
(includes pad entry, padder, 2 beam wash-off stands, dye/alkali pump, 10 beams, rotation stand, cradle let-off stray)	\$ 208,000
Exhaust dyeing 100% cotton only:	
19 atmospheric becks	
1000 pounds capacity each	
cost - \$30,000 each	\$570,000
Installation estimated to be 30%	\$171,000
	\$741,000

Table 3.2-111

Typical Dye Cost for Pad-Batch vs the Same Dyes on Becks [c/pound]

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

All the above costs are for dyeing only (for 100% cotton), not including preparation. All of the beck-dyed costs are cold reactive. In cases where the beck dye would be direct, pad-batch would probably cost more. Beck dyeing will probably cost less.

Extensive work in developing the pad batch system of dyeing cellulose has been done by Cotton Incorporated [27-30]. Some of the following information was developed by them in actual plant experience.

Equipment for the pad batch dyeing consists of:

1. Padding unit
2. Batch or material handling system
3. Dye/alkali mixing device
4. A-frames, storage racks or storage boxes
5. Wash-off device (beam, beck, continuous, etc.)

The padding unit should have the necessary controls for handling the type of fabric that is to be dyed on the unit. In case of knit fabrics, the padder must have adequate guiding, decurling and spreading equipment to handle the knit in open width form. This is especially important on single knit and warp knit fabrics which tend to curl when lengthwise tension is applied. The padder should also have suitable pressure controls to allow the nip to be controlled consistently. A deflection roll padder may be advantageous. Another desirable feature is a small dye trough. This is important to achieve good dye liquor turnover, to minimize the amount of "tailing", and also to avoid reactive dye hydrolysis which might produce shading from beginning to end of the fabric run. A dye trough of ten gallon capacity or less is usually recommended. Adequate speed controls which control the padder and synchronize the hatcher unit are absolutely necessary.

In order to obtain a quality dyeing, uniform from side to side and end to end, the fabric must be uniformly prepared. The fabric should be scoured and/or bleached with a residual pH of 7 or slightly less. It should contain no residual alkali, starch, knitting oils or any other foreign substance which

will interfere with the evenness of absorbency or the subsequent colorfastness of the fabric. The fabrics must wet out rapidly and uniformly and must be uniformly prepared and dried. It is advantageous to make up dye lots of fabrics which were prepared together to avoid possible shade variation within the dye lot.

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

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

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

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

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

There is still another benefit of this rapid fixation. It is a minor point perhaps, and easily overlooked, but there is almost 100% reproducibility from lab to production shades. The pad batch system may be home design, but it must feature accurate in mixing and metering. Two tanks hold dyestuff and alkali solutions which are fed to a mix and dispensing mechanism with a proportioning device. The mix is then fed via a pump to the pad unit. By employing a hollow dispenser, it is possible to keep the passage through which the fabric passes less than one inch wide. This keeps the volume of liquor very low, about eight gallons or less, and insures the rapid turnover of liquor so that dye decomposition is kept to a minimum. This is, of course, important because adding the alkali to increase reactivity also affects the stability of the liquor. (See Figure 3.2-2.)

In working with plant production pad batch units, the following four point checklist has been helpful in avoiding problems:

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

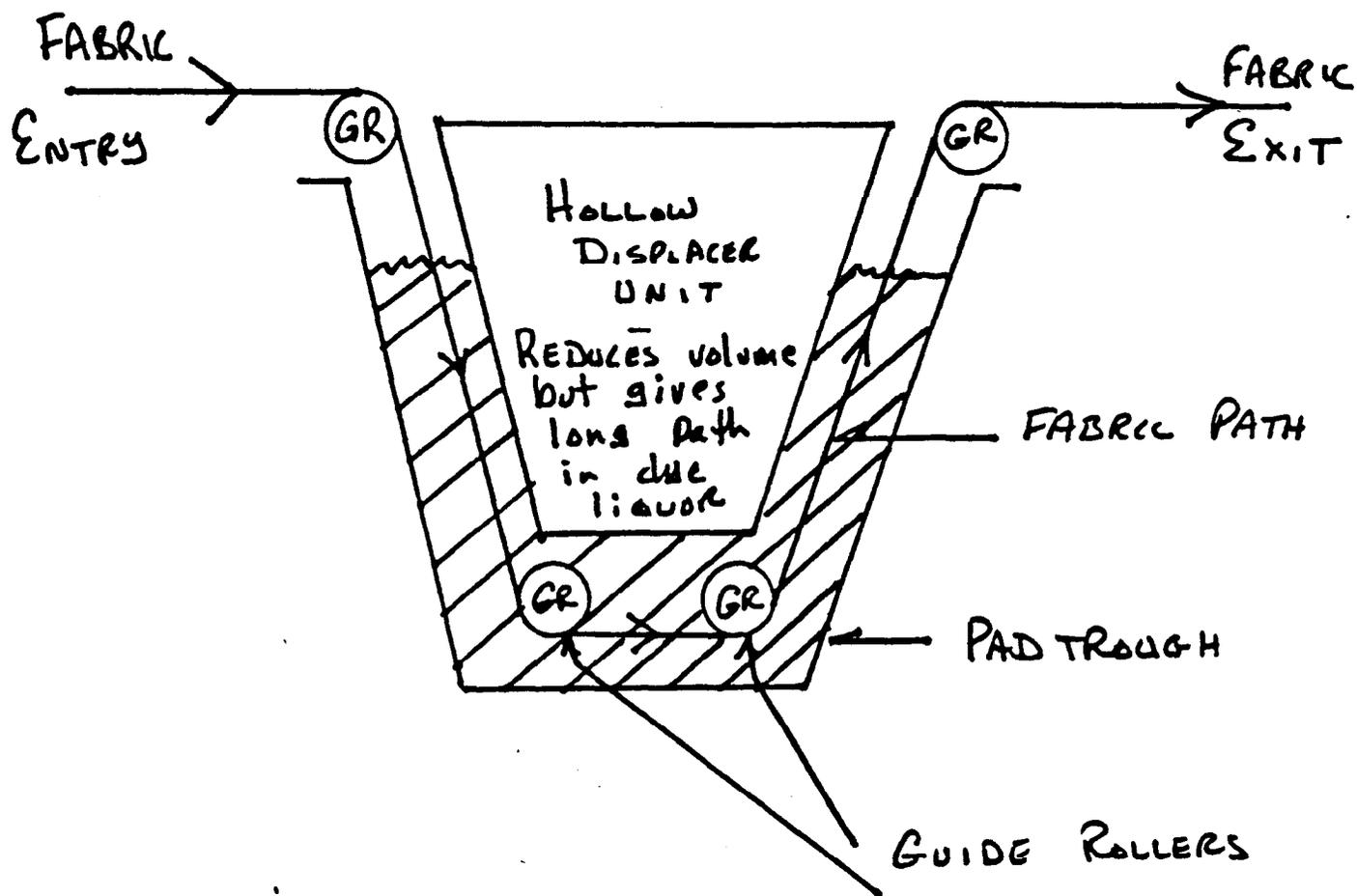


FIGURE 3.2-2 [3.1-2]
PAD WITH DISPLACER

FIGURE 3.2.-2

2. Adjust exhaust dye recipes for pad batch by keeping accurate data on liquor ratios. Keep the immersion long, the liquor ratio short, and the volume low in the pad.
3. Have good preparation. Actually, pad batch reliability has reached the point where it can be used as a check on the preparation. If something doesn't look right, most often it can be traced to mistakes in preparation.
4. Keep good temperature control, especially avoid dyeing hot fabric fresh from preparation. Feed cold fabric to the pad or else the temperature will rise. During very hot weather, keep the mix cool with a cooling water jacket or use ice in the mix.

since many mills that have agreements with municipal sewage systems pay on some formula based on the content of ROD, COD or other undesirable contents of the effluent, the pad batch method employing cold reactives is also attractive from the pollution source management standpoint. Reactives do not require reducing or oxidizing agents, as do vats or sulfurs. Reactive dyes require use of massive amounts of salt when employed in becks, but in the pad batch method, cold reactives require no salt at all.

The use of chemical specialties such as lubricants, leveling agents, antimigrants, fixatives, defoamers and other specialties by pad batch dyeing is usually not required. Small amounts of detergent are used in washing-off.

In summary, excellent results have been obtained with the pad batch (cold) system utilizing high reactivity dyes. Dyers have experienced many benefits:

1. Reduction in waste loads in effluent
2. Low capital outlay

3. Low energy requirements
4. High production speed
5. Reduced labor requirement
6. High color yield
7. Outstanding reproducibility
8. Excellent penetration, and leveling characteristics
9. Rapid fixation
10. Substantial overall cost savings (dyes, chemicals, labor, water, etc.)

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

3.3 Water Conservation

One area that can usually render both cost savings and pollution management through source reduction for textile mills is the practice of water conservation. It is not unusual to find situations where 10 to 20% reduction in water use can be realized.

Commonly observed sources of water waste are:

- . hoses left running
- . broken or missing valves
- . cooling water left running when machinery is shut down
- . defective toilets, water coolers

Several methods have been used to recover and/or segregate waste water streams. Once-through noncontact cooling water can be reused by sending it back to a clear well or influent water line to the mill. This can result in significant water savings.

Waste streams from roof drains and parking lot drains, from cooling water sources, from process waste water, and from domestic waste can sometimes be segregated, treated, and discharged separately to a mill's advantage. Details are usually site-specific.

Most waste water from textile wet processing is from washing operations, primarily in preparation or dyeing. Since preparation processes are typically continuous, well-known techniques such as countercurrent washing can be used to great advantage for water conservation in these washing processes.

3.3.1 Water Consumption of Batch Dyeing Machines

Different types of dyeing machinery use different amounts of water. There are many "low liquor ratio" dyeing machines which are purported to save water. The liquor ratio is the ratio of amount of water (in pounds) in the exhaust dyebath to amount of fabric (in pounds). This differs greatly between machine types. However, most water in dyeing operations is used for washing, and not in the dyebath itself. Thus it is not necessarily true that a dyeing machine with 10:1 liquor ratio will use half as much as a dye machine with 20:1 liquor ratio. Table 3.3.1-I [18] shows typical values for liquor ratios and water consumption for various types of dyeing machinery.

In general, the heating of dyebaths constitutes the major portion of the energy consumed in dyeing; therefore, low liquor ratio dyeing equipment represents major energy savings. But the washing efficiency of many types of low liquor ratio dyeing machines, such as jigs, is poor. Washing efficiency

Table 3.3.1-I

Dyeing machine	H ₂ O consumption [20] gal/#	Typical liquor ratio liquor/goods at time of dye application
Continuous	20	1:1
Beck	28	17:1
Jet	24	12:1
Jig	12	5:1
Beam	20	10:1
Package	22	10:1
Paddle	35	40:1
Stock	20	12:1
Skein	30	17:1

depends on mechanical factors, such as bath and fabric turnover rate or "contacts", liquor ratio, turbulence and other mechanical considerations and physical flow characteristics. Thus, low liquor ratio and reduced total water use do not always correlate as closely as one might expect.

3.3.2 Solvent Processing

At one time, during the 1970s, great interest was expressed in solvent systems other than water for processing textiles. Solvent preparation, dyeing, finishing, and drying were closely examined by the industry. These did not meet wide acceptance due to two factors. First, chemical systems, dyes, specialties, etc. appropriate to solvent use were not available at commercially competitive cost. Second, environmental regulations on airborne emissions from solvent processing equipment, storage facilities, and hazardous waste regulations on recovery byproducts (still bottoms, etc.) made many solvent processes untenable. There are, however, certain instances where solvent processing can be used for source abatement.

3.3.3 Low Add-on Finishing

Foam processing (including mercerizing, bleaching, dyeing, finishing) is being successfully used for water conservation.

Other low add-on techniques, including engraved rollers, kiss-rolls, etc. have been used to reduce water consumption. However, these are mainly used in continuous processes where there is little or no water discharge anyway. There have been some experimental systems for foam dyeing such as the Sancowad process. These can reduce amounts of water used in exhaust dyebaths. As stated previously, this does not necessarily correlate directly to water use reduction.

Wet finish application procedures can be classified into categories:

- saturation/expression
- controlled application

Specific commercial application methods are shown in Table 3.3.3-I [31].

Controlled low add-on processes have individual differences which result in specific advantages and limitations but, in general, advantages are gained in cost, productivity, quality and reduced water and chemical use:

<u>Category</u>	<u>Advantages</u>
cost:	Faster dryer speed
	Less chemical use
	Lower energy use
Quality:	Improved hand
	Better fastness
	Better dimensional stability
Productivity	Faster dryer speed
	Wet-on-wet processing

Other advantages can be realized by specific methods.

3.3.4 Rapid Inverse Dyeing

One water conservation strategy which is widely practiced by dyers of polyester/cotton blended fabrics is rapid inverse dyeing (RID) using disperse and fiber reactive dyes. In the normal process of dyeing these blends, the steps are:

"FORWARD"

- Prepare fabric
- Dye polyester (disperse)
- Wash or reductive after clear

Table 3.3.3-I
Commercial Low Add-on Finishing Processes [31]

Process	Category
Air jet pad	Saturation/expression
Curved blade applicator	Controlled application
Fabric transfer loop	Combination
Gas phase	Controlled application
High extraction pad	Saturation/expression
Kiss roll	Controlled application
Printing	Controlled application
Spray	Controlled application
Stable foam	Controlled application
Unstable foam	Controlled application
Vacuum systems	Saturation/expression
Wicking systems	Controlled application

1 Dye cotton (fiber reactive)

1 wash

The RID process dyes the fiber reactive portion first (on cotton) and utilizes the slightly acidic disperse dyebath as a wash for the fiber reactive. The dyeing process then becomes:

"RID"

- Prepare
- . Dye cotton (fiber reactive)
- . Dye polyester (and wash cotton)

1 Wash or after clear

Other dyeing strategies involve combining the dyeing of two fibers in one bath (disperse/direct) for blends whenever possible, or combining the scouring and dyeing of synthetics or cotton (when strict shade requirements do not have to be met). These are widely practical and vary greatly with end use requirements (shade, fastness, etc.) and specific blends and/or equipment.

3.4 Chemical Screening/Inventory Control

An important part of waste management is raw material quality control. In many cases, undesirable wastes can result from raw material components and impurities that are not actually essential to the process, for example, metal contents of certain dyestuffs. Many companies, such as WestPoint Pepperell, have instituted raw material controls in several stages.

3.4.1 Prescreening

Case History ([3])

The first step in raw material quality control for WestPoint Pepperell's North Carolina plants at Lumberton, Hamilton, Elizabethtown, Fairmont and Clinton includes a chemical prescreening [33].

In 1975 the company established a toxic chemicals committee to review products in use or under consideration and evaluate them according to a wide range of health and environmental impact criteria. The committee has proven to be an effective management initiative which has minimized hazardous waste production and the accompanying costs and environmental impacts.

In 1975, a committee was assembled which included a medical doctor, an industrial hygienist, three research chemists, a professional engineer, a corporate attorney, a corporate safety officer, a representative from chemical production, and a corporate information specialist. In 1976, the committee began its evaluations. It reviewed both chemicals in use and new products considered for use.

Several criteria were used for evaluation in addition to the original considerations of personnel safety and fire hazard potential. These include:

- 1 hazardous waste characteristics
(ignitability, toxicity, corrosivity, reactivity)
- . "priority pollutant" status
- 1 availability of safer alternatives
- 1 biodegradability
- 1 heavy metal content
- 1 potential for accumulation in the facility
- 1 potential for release to the environment
- 1 hazard potential when mixed with other chemicals
- 1 proposed manner of use
- 1 ultimate fate of the chemical
- 1 hazard potential to the customer

Products under use such as hydrazine and hydrofluoric acid were eliminated due to limited ventilation.

Some of the new products considered by the committee and rejected include dichlorobenzidine dyes because of the benzidine base, and a chloride catalyst for resins because of its association with bis-(chloromethyl) ether. Another committee recommendation involved the substitution of a water-based cleaner for organic solvent cleaners.

When it was first organized, the committee scheduled regular quarterly meetings. Part of its function was to establish a set of workable procedures for each plant to follow prior to any chemical purchases. Once these were in place, much of the committee's work could be handled in-plant. Currently, all new chemical purchase requests must be approved by the corporate research center chemist, who follows guidelines set forth by the committee.

WestPoint Pepperell is very satisfied with its chemical safety review program. They attribute their extremely low levels of hazardous waste production to the work of the toxic chemicals committee. They believe their costs are kept lower by controlling chemicals at the point in use and avoiding waste management costs. They currently generate only a small amount of Spent solvent from a dry cleaning operation. The solvent is reclaimed out-of-house by a solvent recovery company.

3.4.2 Routine Raw Material Quality Control

The subsequent quality control of all incoming shipments of dyes and chemicals can be easily done using minimal equipment. One scheme that requires minimum amount of effort on the mill's part and also minimum amount of capital investment is the following:

- 1 Obtain a standard from the vendor for each chemical purchased.

- Perform several simple raw material tests on each drum or shipment of material as it is opened
 - (a) Move the chemical to a normal room temperature environment and allow to acclimate.
 - (b) Retain an appropriate sized sample (100 cc's is usually enough).
 - (c) Check pH with meter or paper and record.
 - (d) Check viscosity with Zahn cup and record.
 - (e) Check density with hydrometer and record.
 - (f) Note color and clarity visually and record.
 - (g) Note odor and record.
 - (h) Check index of refraction with handheld refractometer for clear liquids and record.
 - (i) Compare data to previous history and vendors standard values.

- Retest drums that have been opened for excessively long times.

By using these simple tests a manufacturer can detect significant variations in products which are supplied to him for production use. Examples of the types of commonly occurring anomalies that can be detected are mislabeled drums and changes in the formulation of a chemical specialty.

Chemical specialties are used in almost every textile operation and in most cases, the processor (dyer or finisher) does not know the actual chemical composition that he is using. Suppliers of chemical specialties do not reveal, 'and in some cases do not know, the composition of products they sell. In many cases, the composition of specialties can change without knowledge of the user. Two examples from actual mill experience:

Case I

A manufacturer of a solvent scouring specialty, consisting of emulsifier and xylene, changed the solvent composition to chlorotoluene for cost and labeling reasons when DOT and the vendor's insurance company began to require red labels and special handling for xylene. This had a profound effect on the mill's air emissions, water toxicity, and other aspects of production.

Case II

A vendor of disperse dye carrier formulated a product from emulsifiers, carrier-active solvents and a low molecular weight byproduct from polyester manufacture which was composed of a complex mixture of esters of cresotinic and other organic acids. Because of cost and availability considerations, the vendor changed from one manufacturer of polyester to another for the byproduct. This gave similar (but not exactly the same) dyeing results, but considerably different waste characteristics.

Case III

A chemical manufacturer mislabeled drums of dye fixative as wetting agent, causing massive dye spots.

Any of these situations could have been detected by the simple tests described above.

If the simple tests show unexpected variations in raw materials, then more sophisticated techniques, such as GC and/or IR analysis can be used on retained samples.

Dyestuffs and commodity chemicals can be controlled by techniques described in AATCC methods which are currently available or under development.

It is also a good practice to perform prescreening test protocols on chemicals which have been in use for a long time in order to verify:

- that the chemical use level and practice are correct and reasonable
- that new chemicals and regulations have not made the chemical under evaluation obsolete
- that duplicate chemicals (from a functional point of view) do not exist

3.5 Source Reduction of Metals

Metals are commonly used in textile processing in several ways (as discussed in Section 2.2.1). These include:

- oxidizers for vat and sulfur dyes
- copper aftertreatment for direct dyes
- metal catalyst for resin curing
- special finishes (flame retardant, water repellent)
- dye stripping
- internal distribution system and equipment

Also metals can be brought into processes by the fabric as components of:

- the fiber
- size materials
- fiber finishes
- waxes, oils, lubricants
- dirt or casual contamination of the fabric

This varies over wide ranges, but analysis of two cotton fabrics (after desizing and scouring) showed well over 175 ppm metal content. Typical data are shown in Table 3.5-I for two samples provided by Dr. Jim Rucker of NC State University. These were two 100% cotton fabrics that had been scoured and desized. In addition to these residual metals in the fiber, it is common to find high concentration of metals in processing baths 100 times higher than

Table 3.5-I

*Neutron Activation Analysis of Trace Elements in Cotton Fabric (ppm)

	Sample I	Sample II
Titanium	2.11 ± 5%	< 0.5
Iodine	0.140 ± 7%	0.104 ± 7%
Manganese	1.632 ± 0.5%	1.741 ± 0.5%
Magnesium	7.24 ± 15%	9.80n ± 15%
Copper	2.29 ± 8%	3.16 ± 8%
Vanadium	0.070 ± 10%	0.032 ± 10%
Chlorine	24.16 ± 5%	21.32 ± 5%
Aluminum	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	< 500.00	< 500.00
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

*Data provided by Jim Rucker, NCSU

in the source water. Typical data are shown in Table 3.5-11 for the source water and Table 3.5-111 for the processing solutions.

These metals that are in the source water frequently interfere with the textile process, causing undesirable effects and/or substrate damage, as well as contamination of waste streams. The water sources and most commonly occurring contaminants are:

1) well water

- hardness (Ca^{++} and Mg^{++})
- iron and other heavy metals
- sulfide, carbonate, etc.
- sediment and particulates
- contamination from clear well

2) river water

- as above for well water
- tannic acid (seasonal)
- pollutants from upstream dischargers

3) city water

- all of the above (depends on city's source)
- chlorine
- treatment chemicals
 - . . . copper, alum, etc.
- sediment and other contamination from distribution lines

Internal sources, which can be controlled in order to reduce the production of metal-containing waste streams, include:

1) metals (iron and copper)

- machinery

Table 3.5-11

Analyses of Water from 10 Mills from Georgia and the Carolinas*

Constituent	Equivalency	Concentration of constituents, ppm		
		Average of 10	Range Lowest	Highest
Calcium	CaCO ₃	12.9	1.0	46.5
Magnesium	CaCO ₃	3.8	1.5	7.8
Sodium	CaCO ₃	36.0	5.7	76.1
Alkalinity				
Bicarbonate	CaCO ₃	27.7	10.0	110.0
Carbonate	CaCO ₃	1.4	0.0	10.0
PH		7.2	5.7	7.8
Iron	Fe ⁺⁺	0.1	0.01	0.31
Copper	cu ⁺⁺	0.02	0.01	0.10
Manganese	Mn ⁺⁺	0.01	0.0	0.05
Zinc	Zn ⁺⁺	0.11	0.0	0.24

*Tests performed by Industrial Testing Laboratories, Inc., 2350 Seventh Blvd., St. Louis, MO 63104

Table 3.5-111
 Peroxide Saturator Solutions from Three Mills
 Bleaching Cotton Fabric in J Boxes'

Metal	ppm of dissolved metal in solution ²		
	Average of 143	Lowest	Range Highest
Ca	68.0	28.0	130.0
Mg	24.0	7.7	49.0
Fe	1.5	0.5	3.0
Cu	0.25	0.065	0.68
Mn	0.03	0.01	0.06
Zn	0.49	0.14	0.80

¹H₂O₂, 35% 15-30 g/l.; sodium silicate, .42^o Be., 15-39 g/l

²As metal. Tests performed by Industrial Testing Laboratories, Inc., St. Louis, MO 63104

³From 4 trials in two mills and 6 trials in one mill

- ... containment
- ... feed lines
- ... valves
- copper plumbing
- internal water treatment
 - ... potable/process
 - substrate (plus calcium and magnesium)
- 2) organics, acids, alkalis, and metals
 - live steam (boiler treatment chemicals)

Proper maintenance and the use of alternative structural materials such as PVC pipe instead of copper for plumbing can reduce levels of metals in waste streams.

Finally, there are substantial metal contributions for specific processing situations as identified in Section 2.2. It is possible, for example, to select dyestuffs with low metal contents to reduce discharges of copper, zinc, lead, etc.

The choice of oxidizer systems and aftertreatments for dyes is also important. These are directly related to dye application and are sometimes used to insure complete fixation, insolubilization, or entrapment of the dye within the fiber. An example of this is the use of copper sulfate to aftertreat direct dyes, rarely practiced now in favor of organic resinous fixatives. These resinous fixatives have higher nitrogen content and BOD, but have no copper content. An alternative procedure that avoids both heavy metals and BOD loading is to use epsom salts as a temporary antimigrant until the fixative can be applied from a continuous resin finish formulation.

Also, certain dye classes require oxidation and/or reduction during application and fixing. These dyes (particularly vat and sulfur) were formerly oxidized with dichromate, but are now almost universally oxidized with other materials such as iodate, bromate, or peroxide.

Finally, repair procedures for many classes of dye can involve the use of metals and/or other toxic materials. One type is the zinc sulfoxylate-formaldehyde type of dye stripping agent used on some classes of dyes. This type of repair procedure can contribute to zinc content of waste streams. Another common type of stripping procedure for resin finishes is oxalic acid. This material is known to be toxic. A stripping procedure involving phosphoric acid and urea is equally effective for most resin finishes and with much lower toxicity. The above stripping procedures are for fabric, but one source of toxic stripping agents that is sometimes overlooked is machine cleaners. The cleaning processing frequently are not controlled to the same extent as the dyeing process, and frequently they can contribute to discharge of toxics.

Stripping procedures that are most frequently used in removing unwanted colorant materials from textile materials are:

Stripping Procedures . . . 200F unless otherwise stated

- 1) 2% caustic and 2% hydro, 45 minutes
- 2) 5+% textone at pH 3.5 for 45 minutes (sodium nitrate helps prevent corrosion of equipment)
- 3) 3% hypochlorite at pH > 8.5 (or at pH < 5) 30 min, 160F
- 4) 6% zinc/sulfoxylate/CH₂O and formic acid (pH 4) for 45 min
- 5) Add 10% dye carrier to any of the above and go to 250F
- 6) 4% permanganate at pH 3

The use of the zinc sulfoxylate formaldehyde and/or permanganate can produce zinc and manganese in the waste. Also, the use of textone (sodium chlorite) and/or hypochlorite can cause equipment erosion and dissolve metals that compose the machine. The use of hydro and caustic wherever possible should minimize metal contamination of waste streams.

One other management strategy that can frequently be used to reduce the metal content of wastes is the proper handling of metal containing finish mixes. Residual unused portions of finish mixes are usually discarded as waste. Essentially all finish mixes will contain magnesium and/or zinc catalyst, and many special finishes contain other metals.

One abatement reduction is to make up the new chemical finish mixes by adding to the old ones, thus utilizing the formerly wasted materials and saving cost. Also, planning properly so that excessive amounts of chemical mixes are not left over is important. The calculations required to make adds to processing mixes (as opposed to dumping unused portions) can be facilitated by the use of Pearson's Square. This procedure is described in detail in the literature [53].

4.0 RECYCLE/REUSE/RECOVERY

Source reductions cannot always be accomplished by elimination of chemicals. For example, if cotton is to be prepared properly, alkali must be used. No substitution is possible. In these cases, management strategies must focus on:

- Recycle
- Reuse
- Recovery

4.1 On-site

Recovery systems are used to extract various components of waste streams. Commercial systems include:

- Heat recovery
- Caustic recovery
- Size recovery

The easiest systems to adapt to recovery are continuous processes such as mercerization and continuous washing. Wastes from these are usually continuous flow streams of fairly constant characteristics.

Batch processes are not as easily handled. There are techniques to recover heat, for example, from dye waste from becks and other equipment. Examples of recycle/reuse of chemical products are site-specific. Dyebath reuse as well as chemical and heat recovery are discussed in later sections of this report. Several brief examples of recovery/reuse are given here to indicate the type of situations that have application [321]. All are actual mill production situations.

Case History #1

A manufacturer of delicate lace must dissolve an acetate yarn which has been used to stabilize the lace during processing. He dissolves it in acetone. He then sells the acetone/acetate solution to an acetate producer for regeneration of the acetate and recovery of the acetone. The lace manufacturer gets, in return for his acetate/acetone waste material, clean acetone and acetate fiber. He pays only the cost of the separation process.

Case History #2

A manufacturer of towels uses a yarn made from a twistless cotton core with a polyvinyl alcohol (PVA) wrapper fiber. The PVA wrapper is dissolved in water after the towel is made, leaving a luxurious twistless yarn on the towel surface. The PVA/water waste product is processed to recover the PVA waste and to regenerate the PVA fiber.

Case History #3 [32]

American Enka Company is a nylon yarn production and research facility. One of their processes uses isopropyl alcohol as a solvent for a fatty amine. The end product is a porous film of polymer. They previously employed an outside firm to distill their waste isopropyl alcohol. They then bought it back for reuse in their production line. Average distillation losses were 15%, but losses as high as 40% had occurred. Also, due to improper cleaning of the distillation column between runs, the isopropyl alcohol returned was often unusable due to contamination with Dowtherm, benzene, ethyl benzene, methyl benzene, various chlorinated hydrocarbons, and other organic constituents. Each batch of recycled isopropyl alcohol had to be analyzed for contamination and, if found unsuitable, required disposal arrangements and fees.

To solve this problem, American Enka purchased a used distillation unit for \$7500 and modified it to redistill the isopropyl alcohol in-house. This resulted in a savings of \$90,000/year, since it is less expensive to distill the alcohol on-site than to contract these services. In addition, the in-house distillation is more efficient, recovering 90% of the isopropyl alcohol as opposed to the outside firm's efficiency of 85%. Not only does American Enka reuse the pure isopropyl alcohol the distillation unit produces, but they also utilize the still bottoms as an asphalt emulsifier in another product line. The payback period for this project was approximately one month.

One final common example of on-site waste recovery is the recovery of perchloroethylene cleaning solvent by distillation. This reduces the amount of hazardous waste products by a factor of 10 to 100 and saves the cost of using fresh solvent for each dry cleaner load.

4.1.1 Heat Recovery

An excellent review of waste water heat recovery was presented recently [33]. The following summarizes the details of waste water heat recovery systems and their application to textile waste streams. Most textile processors are familiar with waste water heat reclamation systems of some type. The amount of potential or actual dollar savings is often not appreciated, however.

The number of firms that still do not have reclamation systems or let existing ones lie inoperative for long periods of time is surprising. One of the nation's largest textile firms did not start to put waste water heat reclaiming into effect until just recently even though the unsophisticated laundry industry has been reaping its savings for over 30 years.

The Magee Carpet Company installed an 800 GPM reclaim system before 1957. If this 48,000 GPH unit had been in operation for the last 25 years at a conservative 80 hours/week, 50 weeks/year, while raising the incoming average 550°F water to 100°F, at an average cost of 20¢/gallon for #2 fuel oil for the period, the system would have saved the company a conservative \$3.9 million. This on an approximate \$10,000 investment at that time. If they are presently paying 95¢/gal for the fuel, it represents an annual savings of \$740,361. In addition, the steam not produced to heat the water is equivalent to more than 700 boiler horsepower.

There are several types of heat recovery system designs that are currently in use.

4.1.1. a The "Once-Through" Approach

Many systems use a once-through flow of water for heat recovery. Typically, the hot waste water flows to a large sump which has a varying level. The sump pump is usually controlled with level sensors which cycle the system off at a low level. The length of intermittent off periods is determined by the size and periods of dumping inactivity of the becks. The waste water is pumped out of the pit through the reclaimer and then to the sewer. This design has some drawbacks. First, depending upon the flow and temperature of the incoming water to the other side of the heat reclaimer, the exiting waste water may not be "cold". This is especially true if the next scheduled beck dump in the recipe is to be a "cold" one. Just because the waste water has already been through the exchanger does not mean that it no longer contains recoverable BTUs. The once-through concept also assumes that the fresh water flow matches that of the waste water, which does not in fact occur. Next, when there are few or no dumps and the sump level falls to the

cut-off point, there obviously is no BTU recovery. Because of the varying level, it is also necessary to position the pump suction at the low point of the sump. This also happens to be the location of the coldest water in the sump. At the cut-off level, the hottest water remains in the pit.

4.1.1.b Stratified Sump

The stratified sump type system is an improvement based on the fact that heated water will stratify. This allows the sump to release the hottest water available for BTU recovery and to waste the coolest water when excess is present. This is accomplished by a series of underpass and overpass dams. The holding pit is deep and the liquid waste is maintained at the constant level.

When a "cold" dump enters the pit, if it is relatively colder than water presently there, it will sink to the bottom and be the first rejected. If this "cold" dump is warmer than what it encounters, it will float to the top and the BTUs it carries are now available for reclamation.

This establishes a constant level with the hottest water trapped behind the underpass dam and at the top; the system operation can be designed to operate continuously at a fixed flow rate (thus permitting the most economical exchanger selection for good heat transfer). All equipment is based upon this steady average flow consideration, not on a quantity of water in a pit that must be handled before the next dump (at best an assumed value for most plants) on a once-through method. Pump suction is positioned where the hottest water is at the top. During periods of no dumping activity, the system continues to extract BTUs, though obviously not at the same rate. The system thus maximizes heat reclamation regardless of process demand or temperature.

Heat reclamation systems are frequently plagued by plugging due to lint and other sediment that comes from processing of fibrous materials. Therefore, lint screens in dyeing machines, bar grates, and other primary control methods must be maintained to insure proper operation. Also, the design of the reclaimer itself can include anti-fouling features, such as timed backwashes, etc.

Perhaps the easiest streams on which to practice heat reclamation are streams from washers and other continuous equipment. This can frequently be done without the complicated sumps, level controls, and other devices required for batch dumps.

Case History #1 (32]

A case history for heat recovery has been published for Ellen Knitting Mills, which was discharging spent dye bathwater to the municipal sewer system. The temperature of the discharge water was 130°F which caused breakage of the terra cotta sewer piping. In 1981, the company invested \$100,000 in a heat exchange system that lowered the effluent water temperature to 70°F. Spent dye water is discharged into a holding vat from which it enters the stainless steel heat exchanger. The exchanger is composed of five 30 ft. long 8 in. diameter pipes. Inside each pipe is a bundle of smaller tubes which allow the heat transfer.

Heat removed from the water is used to preheat incoming feed water for the dye tubs from 55°F to about 105°F. The preheating operation saves about 52,000 gallons of fuel oil per year, and the heat exchange system had a payback period of only two years.

Case History #2 [34]

Russell Corporation improved its conversion efficiency of steam from boilers to hot water for its bleachery by installing back pressure regulating valves to control return line condensate. This reduced the amount of condensate which flashed into steam and returned higher temperature condensate to the boiler. Each 10°F rise of boiler feedwater results in a 1% fuel savings. The total savings to Russell was \$1000 per day.

4.1.2 Size Recovery

Size represents the largest single group of chemicals used in the textile industry [35], and they do not become a permanent part of the product, in most cases. Therefore, size recovery represents perhaps the greatest opportunity for recovery of any chemical group. This is most convenient in vertically integrated mills where the recovered size can be returned directly to the slashing operation make-up kettles. The common types of sizes used on textile warp yarns are:

Starch

Carboxymethyl cellulose (CMC)

Polyvinyl alcohol (PVOH)

Polyacrylic acid (PAA)

Polyvinyl acetate (PVAc)

Polyester (PET)

Modified cellulose and starches

By far the most common is starch. It is removed from textile substrates by degradation by the action of acid or enzyme. Because it is degraded, no recovery is possible. The other types are more or less recoverable. The molecular size, water solubility and other factors which influence

recoverability are controlled by the molecular structure, particularly the molecular weight and substituents that are added to the polymeric chain. These substituents are used to control adhesion, film forming and penetration properties, removability, and other important features relating to the functional behavior of the size.

The recoverable sizes, primarily PVOH, are more expensive than starch. Thus it is difficult for a nonvertical weaver to use these more expensive sizes so that another independent processor can recover them at a later time. Also, it is difficult for a nonvertical wet processor to buy expensive recovery equipment in hopes that the weaver will use a recoverable size. Therefore, size recovery systems are found typically in vertical operations such as Stevens, Milliken, and Springs [36].

Typical size recovery scheme is shown in Figure 4.1.2-1.

4.1.3 Caustic Recovery

The recovery of caustic from mercerizing operations is also practical. Mercerization is the process of treating cotton fabrics and certain blends with concentrated (approx. 15% or more) sodium hydroxide solution. Waste streams from this process are extremely alkaline. Because mercerization is always a continuous process, these waste streams are fairly easily handled. Recovery systems can reclaim up to 98% of the caustic used [36].

One system that avoids the use of caustic (and also water) in the mercerization process is the use of liquid ammonia. This produces the same effect as mercerization without the highly alkaline waste water stream. Of course, the ammonia gas is recovered and reused.

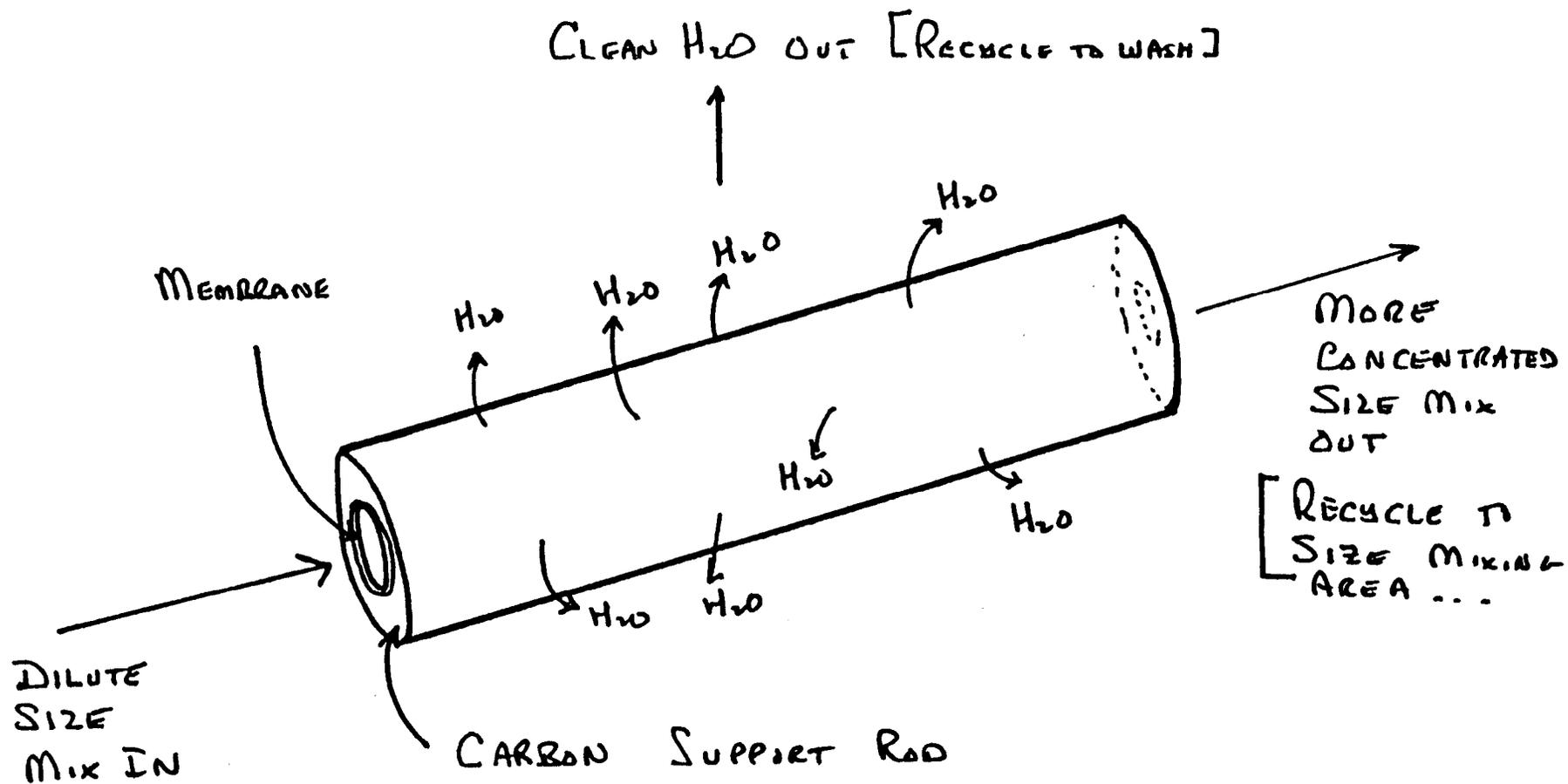


FIGURE 4.2.1 -1

SIZE RECOVERY

4.1.4 Dyebath Reuse

The idea of dyebath renovation and reuse began attracting attention around the middle 1970s when energy costs became a critical factor in overall manufacturing costs. Dyebath renovation and reuse has been shown to be an effective method of cost reduction, energy savings, and pollution source reduction in textile wet processing. Laboratory studies, pilot plant work, and full scale commercial use have been documented. This report summarizes these documented studies and presents typical examples of comparative procedures.

In 1964, it was estimated that about 10% to 16% of textile wet processing waste waters were reclaimed or recycled [37]. Modern water and energy conservation practices, including strategies such as dyebath reuse, make it possible for wet processors to increase this figure dramatically, with corresponding cost savings and pollution abatement.

Dyebath reuse can be and is an attractive alternative to pretreatment systems for dyehouses that discharge to POTWs. In many cases, dyehouses operating in cities do not have enough space to construct large pretreatment systems. Dyebath reuse, which has been shown to reduce flow, BOD, and COD loadings by up to 33%, requires a smaller investment in equipment than pretreatment systems [38]. Also, the dyebath reuse concept has a return on investment in the form of dye, chemical, and energy savings which pretreatment does not.

Savings that result from dyebath reuse, as well as installation costs and operating expenses, are site-specific. Based on case histories available to date, the data in Table 4.1.4-I generally summarizes the magnitude of these factors.

Table 4.1.3-I

Typical Cost and Savings Figures for Dyebath Reuse per Dye Machine [37]

Lab and support equipment (one set required)	\$ 9,000
Machine modifications, tanks, pumps, pipes	15,000 to 25,000
Annual operating costs	1,000 to 2,000
Annual savings (total)	21,000
Dyes and chemicals	15,000
Water	750
Sewer	750
Energy	4,500

4.1.4.a Dyeing Processes Generalities - Chemicals, Dyes, etc.

Typically, an exhaust dyebath will contain some or all of the chemical components shown in Table 4.1.4.a-I.

Typically, only the dye and, to a lesser extent, a few specialty products are exhausted during conventional dye processes. Most of the chemicals remain in the dyebath and are discarded with it. Reuse saves the cost and pollution associated with discharge of those chemicals in the spent dye liquors, and it also saves the energy required to heat the dyebath up from the fill water temperature to the appropriate starting temperature for the next dyeing.

Savings amounts for energy, chemicals, BOD, COD, pH and hydraulic loading of waste streams vary with amounts and types of specialities that are used. These in turn depend on many factors, including the shade being dyed, dye class, color specification (fastness, critical shade match, etc.), equipment, fabric construction and fiber content, and other factors. Some of these will be reviewed in specific cases for each dye class, but some general comments can be made about dyebath components at this time.

Dyestuff (colorant content) is exhausted to a large extent, usually 90 to 95%, onto the fiber. For some dye classes, this involves an approach to equilibrium governed by thermodynamic and kinetic laws without chemical alteration of dyestuff during the process. Establishment of such equilibria is governed by factors such as pH, temperature, liquor ratio, concentration of electrolytes, etc. This is true for acid, basic (cationic), direct, and disperse dyes. In contrast, certain other dye classes undergo chemical reaction during the dyeing process and are therefore conceptually different from the above mechanism. These dyes are typically rendered insoluble, reacted, or entrapped in the fiber in a form that is chemically different from

Table 4.1.4.a-I
Components of a Textile Dye Bath

Water

Dyestuff (colorants)

Buffer system/pH control

Electrolyte (common salt or Glauber salt)

Specialty dyeing assistants, such as

... retarder/accelerant

... leveling agent

... lubricant

... defoamer

... surfactant/dispersant

... sequesterant

... other special purpose chemicals

the original form in the dye liquor. Examples are fiber reactive, naphthol (azoic), sulfur, and vat dyes. In such situations, experience with dyebath reuse is not as well documented, although it may be possible to practice dyebath reuse in these cases also.

In any case, dye as it is added to the dyebath is not 100% pure colorant. Commercially, colorants may be cut typically 20% to 80% with various diluents typically which do not exhaust. Because the dye concentrations in the bath are low (typically under 1000 ppm), diluents build up slowly in reused dyebaths over many cycles and are not a severe problem. Diluents vary with dye class, but include surfactants, dispersants, common salt, Glauber salt, soda ash, and other materials that do not usually exhaust.

Buffer systems for pH control include organic acids such as acetic and formic, as well as inorganic salts. Mineral acids are occasionally used. These are usually not depleted except in proportion to the amount that is lost as water is carried off by the substrate (fiber, yarn, fabric). In some cases, where organic acids are used, substantial COD and BOD reductions can be made by dyebath reuse. Alkali systems are typically materials with little or no BOD contribution, such as caustic, soda, ash, TSP, and TSPP, and these can be saved for dyebath reuses.

Electrolytes, primarily common salt and Glauber salt, are typically not exhausted. Although they do not contribute to BOD and COD loads, they can be present at concentrations of over 10,000 ppm in the dyebath for some shades, and can create problems in waste treatment by inhibiting oxygen transfer in aeration, especially under shock loading conditions. Dyebath reuse can save essentially all of these materials except the proportion that is lost with dye liquor that is carried off in the substrate.

Retarders vary greatly in their exhaustion characteristics. Some act almost exclusively on dye in the solution, while others act primarily on the fiber itself. The latter types are essentially 100% exhausted during the dye process. In many cases, separate retarder is not used; rather dye exhaust rate is controlled by pH, temperature, electrolyte concentration and other process variables.

Accelerants, especially dye carriers for disperse dyes on polyester, vary greatly in their exhaust characteristics. These dye carriers typically are blends of organic solvents and surfactants. Components of such mixtures usually exhaust at different rates and can cause an imbalance in the dyebath after many reuse cycles. Also, the components of the carrier-active blend may vary in volatility, causing losses from open dye machines to the air. The BOD loads associated with dye carriers is discussed in the first section of this document.

Leveling agents for disperse dyes on polyester generally exhaust less than carriers discussed above, but are otherwise similar for purposes of this presentation. Leveling agents for other classes (acid, basic, and direct) generally work in the dye liquor and are not exhausted.

Surfactants and dispersants do not usually exhaust. In fact, the concentration of surfactants can be expected to increase with reuse cycles due to the accumulation of unexhausted portions of materials such as dye diluents, retarders, accelerants, levelers, lubricants, and fiber finishes. These may eventually cause significant changes in dye exhaust rate, retarding of dyeing, and lower ultimate exhaustion of dyebath if allowed to build up too much. It is impurities like this that limit the number of times as a dyebath can be reused. The number of reuse cycles varies for each specific dye/fiber

situation; however, in general, most dyebaths can be reused at least 5 to 10 times, and few can be reused more than 20 to 25 times in commercial situations.

Lubricants such as mixtures of surfactants and other materials (like butyl stearate) typically exhaust and must be at least partially replaced for dyebath reuse as part of the renovation procedure.

Defoamers, sequesterants, and other specialities are used on as-needed basis in small amounts, and are not generally lost.

4.1.4.b Methods

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

2. Analyze or estimate the dye and chemical content of spent dye liquor using a spectrophotometer and/or guidelines based on specific production experience. Equipment for this is commonly available at a cost of under \$10,000 (see Table 4.1.4.b-I).

unexhausted dyestuff is measured by solution coloristic techniques, sometimes using extraction techniques if the bath is turbid. Extraction solvents include 1-octanol for basic and acid dyes [47] and toluene for disperse dyes [48].

Table 4.1.4.b-I
Dyebath Analysis Equipment [48]

Equipment required	Quantity	Source	Catalog number
25 ml graduated cylinder	2	(1)	08-550C
25 ml sample (separatory) funnels	2	(1)	10-437-10C
20 cc glass syringe	2	(1)	14-823-10D)
Ring stand and rings	1	(1)	14-670C, 14-052B, and OS-738
Cotton stand and rings	1	(1)	-
Table salt	1 pound		-
Solvent	4 liters	(1)	-
Sample cells	4	(1)	14,385-912B

(1) Fisher Scientific Company, Atlanta, Georgia (404) 449-5050
Approximate cost (1983) \$350

Chemical losses are determined by specific production experience based on losses due to exhaust, volatilization, and dye liquor carry-off with the dyed substrate (usually about 10 to 15%). Chemical losses may be estimated or determined analytically if appropriate equipment is available. Usually the quantities are not as critical as the dye, and an estimate is sufficient.

The procedure for extracting dye from the dyebath is as follows:

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

3. Add make-up amounts of ayes and chemicals to renovate the spent bath.

Also add water to make up the volume that is carried off by the dyed substrate.

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

of dyebath reuse. The ultimate "life" of a dyebath varies according to the quality required, contaminant buildup, and other factors [41].

4.1.4.c Dye Classes and Potential for Bath Reuse

There are many different classes of textile dyes, and each class applies to specific fiber types and requires different exhaustion procedures, specialty, chemicals, pH, equipment, etc. Because of these differences, the savings that can be expected vary. Also, results may vary in respect to the fastness, shade reproducibility, and other factors. Batch dye systems have been reported to be adaptable to dyebath reuse as shown in Table 4.1.4.c-I [40].

Specific case histories are cited for several dye/fiber classes, including acid/nylon, basic (cationic)/Nomex, and disperse/nylon under case histories.

No case history has been published for direct dyes on cellulose; however, this could also be done. This would result in chemical savings of salt, leveler/retardant, dye, surfactant, lubricant, and defoamer. Dyebath reuse would likely be limited by contaminant buildup of two types.

1. Fabric impurities not removed during preparation
2. Emulsifier systems wetters and dispersants from dye, retarder, etc. These should be of fairly minor importance, and dye reuse should be possible for 15 or more cycles.

A laboratory study of reuse of disperse dyes on 100% polyester spun yarn (package dye) showed that nine reuse cycles could be expected, with savings of about 80% on water and chemicals, and about 40% on energy [45].

4.1.4.a Limitations

To gain the maximum benefit from dyebath reuse, users must keep certain considerations in mind.

Table 4.1.4.c-I
Systems for Dyebath Reuse [40]

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

The easiest systems to manage for dyebath reuse are dye classes that undergo minimum chemical changes during the dyeing processes. These are:

1. acid dyes for nylon and wool
2. basic dyes for acrylic and certain copolymers
3. direct dyes for cotton
4. disperse dyes for synthetic polymers

A higher degree of difficulty can be expected from other classes.

The easiest situation to manage is the reuse of a dyebath to repeat the same shade with the same dyes and equipment on the same fiber. It is also possible to reuse a dyebath to produce a darker or lighter shade with the same dyestuff selection on the same fiber. More difficult situations would involve addition of new colorants to renovate a dyebath. This would lead to potential problems with shade matching and metamerism.

The number of cycles that a dyebath can be reused is limited by buildup of impurities [41]. These impurities can come from several sources. One source is fabric impurities from incomplete preparation, which include natural impurities in cotton and wool, knitting oils, winding waxes and emulsions, fiber finishes, size materials-and the like. Impurities can also accumulate from dye diluents, salt buildup from addition of acids and bases for pH control, steam impurities for direct steam heated baths, and emulsifier systems from exhausted specialties. Many impurities are surfactants, and these can cause stripping and/or retarding of dye exhaust if allowed to buildup excessively. Other problems such as spotting and excessive foaming can occur if too many reuse cycles are attempted. The usual range of reuse cycles is 5 to 25, and each process and/or shade must be optimized by actual production experience.

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

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

In summary, batch dyebath reuse may not be for every situation; however, the economic savings are large, if properly applied.

4.1.4.e Case Histories

Case History #1

Perhaps the most extensive and best documented study on dyebath reuse was carpet dyeing done by Bigelow in the summer of 1983 [38,39,47,48]. In this work, carpets were dyed with conventional (Procedure I-A) and with dyebath reuse (Procedure I-B). Results of quality, savings, and pollution abatement were carefully documented in detail. Some of the more interesting data relating to pollution abatement show that BOD and COD were reduced by over 30%, and phosphorous, phenolics, and total dissolved solids were reduced by 50% and 80% (see Table 4.1.4.c-II).

Dyeings in Bigelow production runs were done on two different shades and styles of carpet. A pair of conventional atmospheric becks were used, and dyebath was pumped back and forth between them. Over twenty reuse cycles

Procedure I-A

Conventional Carpet Dye Procedure [47]

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

Procedure I-B

Modified Procedure for Carpet with Dyebath Reuse [47]

-
1. With beck drain open, load two rolls of carpet onto beck using spray rinse (tint added to greige carpet is removed from carpet yarns during spray rinse; for reconstituted dyeings, the drain is left open to prevent tint buildup in recycled dyebaths).
 2. Close drain. Arrange and connect dyebath transfer equipment into appropriate orientation. Set flowmeter totalizer to zero. Pump dyebath to new beck from beck used for previous dyeing.
 3. Add auxiliary chemicals to beck; continue mixing for five minutes after all chemicals have been used.
 4. Measure pH and adjust if necessary.
 5. Add dyes and mix for ten minutes.
 6. Raise dyebath temperature to 180⁰F at 3⁰F per minute.
 7. Dye at 180⁰F for 30 minutes.
 8. Sample and, if necessary to obtain acceptable dyeing, perform add(s). (After each add, run 15 additional minutes.
 9. Add cold water with beck drain closed and cool to approximately 140⁰F. (Some exhausted dyebath will be lost through overflow ports.) Collect dyebath sample for absorbance measurement. Pump to new beck (Step 2 of subsequent dyeing cycle). Perform solvent extraction of dyebath sample, perform absorbance measurements and calculate amount of dyes and auxiliary chemicals required for next dyeing. Drain.
 10. Close drain and fill beck, cold water to rinse, cool, and float carpet.
 11. unload carpet. Drain and flush beck to prepare for next dyeing.
-

Table 4.1.4.c-II
 Pollution Reduction Results
 Dyebath Reuse for Carpet [47]

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

Pollutant	Conventional	Pollutant loading Carpet style I Dyebath reuse	Reduction
Pollutant			
BOD (g/kg)	22	14	36%
COD (g/kg)	80	54	32%
TSS (g/kg)	0.2	0.14	30%
TDS (g/kg)	40	21	48%
Phenolics (mg/kg)	0.8	0.15	81%
Total-P (g/kg)	1.9	0.5	74%

occurred. Savings were estimated to be over \$60,000 per year per pair of becks.

Case History #2 [40]

Adams-Millis company has practical dyebath reuse in plants at High Point and at Franklinton, NC. In both cases, nylon pantyhose were dyed in rotary paddle machines with disperse dyes. The results were so good that 95% of the rotary drum machines at the Franklin plant are reportedly running dyebath reuse systems. The idea of reuse was also used in these operations in another way.

The final softener bath is reused as a prescour for the next batch to remove oils, fiber finish, etc., before dyeing. Cost savings are estimated at 2¢/lb of goods produced. Conventional and reuse procedures are shown (Procedures II-A, B and C).

Case History #3 [40]

Evans & Black (E&B) Carpets instituted dyebath reuse at its Dalton, GA, plant for the disperse dyeing of nylon carpets. The result was a projected savings of \$115,000 annually to the mill using eleven becks.

This study shows that exhaust levels occurred from the dyehath as shown in Table 4.1.4.c-II.

At this time, 45% of the plant's production is dyed with reused baths. It was confirmed in this production situation that buildup of surfactants during the repeated reuse cycles causes slight decreases in the disperse dye exhaust. This is only a minor problem and can be compensated in general by increasing the dye concentrations slightly as reuse cycles increase.

Procedure II-A

Disperse Nylon

Conventional Adams-Millis Procedure for Dyeing Pantyhose [40]

Step

1. Fill with cold water.
2. Add auxiliary chemicals, run 3 minutes.
3. Raise temperature as rapidly as possible to 160F.
4. Add disperse dyes, start basket turning.
5. Run machine 2 minutes.
6. Load goods evenly while turning machine downward into bath.
7. Run 45 minutes at 160F.
8. Sample; make add if necessary.
9. Dump the bath.
10. Refill with cold water.
11. Inject steam rapidly to reach **110F**.
12. Add finish chemical and run **10** minutes at 110F.
13. Dump the bath.
14. Unload the pantyhose.

Approximate running time (zero adds) = **1** hour 40 minutes (**100** minutes)

Procedure II-B

Disperse Nylon

Reuse Procedure With Prescour for S-cycle and 17-cycle Sequences (40]

Step

1. Load goods evenly to machine full of softener water from previous cycle.
 2. Run for 5 minutes.
 3. Drop prescour bath to drain.
 4. Unload wet hose from machine.
 5. Drop dyebath into machine (130-140 gallons).
 6. Add water until 160 gallons reach on sight glass.
 7. Raise temperature as rapidly as possible to 160F with rotation.
 8. Add auxiliary chemicals.
 9. Add dispersed dyes.
 10. Run 2 minutes.
 11. Reload goods evenly while turning downward.
 12. Run 45 minutes.
 13. Sample; make add if necessary.
 14. Sample dyebath for analysis.
 15. Pump dyebath to holding tank and drain residual water in machine.
 16. Add 160 gallons water (fill to 200 gallons on sight glass).
 17. Raise to 110F.
 18. Add finish chemical.
 19. Run 10 minutes.
 20. Unload goods
 21. Return to Step 1.
-

Procedure II-C

Disperse Nylon

Reuse Procedure Without Prescour for 14-cycle Sequence [40]

Step

1. Drop dyebath into machine (130-140 gallons).
 2. Drain side pipe.
 3. Add make-up water to 190 gallons on sight glass.
 4. Add steam to 160F.
 5. Add auxiliary chemicals.
 6. Add disperse dyes (plus 3 gallons water).
 7. Load goods (dry).
 8. Run 45 minutes at 160F.
 9. Sample; make add if necessary.
 10. Sample dyebath for analysis.
 11. Pump dyebath to holding tank.
 12. Add 160 gallons of fresh water (to 200 gallons on sight glass).
 13. Raise to 110F.
 14. Add finish chemical (plus 3 gallons water).
 15. Run 10 minutes.
 16. Drain softener bath.
 17. Unload goods.
 18. Return to Step 1.
-

Table 4.1.4.c-II

Exhaust from Dyebath Nylon Carpet/Disperse Dye Becks [38,43]

Dye - 90%

Carrier - 50%

Leveling agent - 25 to 50%

Other components - Proportional to water loss

Case History #4

Basic dyes are normally exhausted from acidic baths for acrylic and certain other copolymer materials. One case history relating to dyeing basic dyes on Nomex in jet dyeing machines is available [43].

In these evaluation trials, dyebaths were reused up to 15 times successfully. Capital expenses to install the equipment necessary to accomplish dyebath reuse were determined to be about \$15,000. Savings were estimated to be \$120 to \$140 per dye cycle (500-700 lbs) for a cost reduction of 17 to 28¢ per pound. The annual savings to the mill was estimated at \$100,000.

In this data, like the Adams-Millis study, there was uneven depletion of various components of dye carrier during the dye process. This required a reconstitution of 65% for dye carrier compared to 10% for other chemicals.

Case History #5

Acid dyeing of nylon carpet [43] using reconstituted dyebaths was done on atmospheric becks. Dyebath reuse was limited to 10 cycles due to buildup of salt. This led to an annual savings estimated at \$31,300 compared to a total cost of \$15,000 for installation of necessary equipment.

Procedure III-A

Traditional Dyeing Procedure for Nomex Type 455 [43]

Step**Dyeing**

1. Fill dyeing machine.
 2. Load fabric.
 3. Add to bath at 10F (38C):
1% surface active agent (Merpel HCS)
20 g/l. carrier (Dymex)
 4. Run 5 minutes.
 5. Add cationic dyes which have been pasted with acetic acid and dissolved in water.
 6. Run 5 minutes.
 7. Add in three parts over 20 minutes, 20 g/l. sodium nitrate.
 8. Adjust pH to 3.5 to 4.0 with either TSPP or acetic acid as required.
 9. Raise to 250 F (121C) at 3F (1.7C)/minute.
 10. Run 1 hour at 250F (121C).
 11. Cool to 150F (66C) and sample; dye adds should be run at least 1 hour at 250F (121C) to insure penetration.
 12. Cool to 120F (49C) and drop bath.
 13. Rinse clear at 120F to 130F (49-54C).
-

Procedure III-B

Modified Dyeing Procedure for Nomex Type 455 for Dyebath Reuse [43]

Step

Dyeing

1. Fill dyeing machine with reconstituted bath.
 2. Load fabric.
 3. Adjust pH to 3.5 to 4.0 with either TSPP or acetic acid as required.
 4. Raise to 250F (121C at 3F (1.7C/minute))
 5. Run 1 hour at 250F (121C).
 6. Cool to ISOF (66C) and sample; dye adds should be run at least 1 hour at 250F (121C) to insure penetration.
 7. Cool to 120F (49C) and pump bath to holding tank.
 8. Rinse clear at 120F to 130F (49-54C).
-

4.2 Waste Reuse

The idea of reusing can be extended beyond in-house reuse. For example, a waste stream that commonly is produced from pickling of agricultural products is 17% acetic acid. This product has been filtered and used in textile dyeing to provide the required acidity in disperse dye baths. Usually, the mill would use 56% acetic acid, so the dye recipe must be adjusted to use about three times as much of the 17% acetic acid. (Save the cost of 80,000 #/day of 56% acetic!)

Textile manufacturers located close to furniture mills can frequently obtain large quantities of wood scraps for their boilers. This eliminates wood scrap waste from furniture mills and it saves fuel cost for the textile mill.

In another case [32] Eileen Mills was able to purchase and install a sawdust-fired steam generating plant for approximately \$800,000. The unit consists of a 12 ton receiving hopper, a conveyor transport system, a hogger, a 200 ton storage silo, a dutch oven combustion chamber, an auxiliary oil burner, and a 400 horsepower HRT boiler.

In the vicinity of Spruce Pine, NC, there are several local sawmills and a ready supply of waste sawdust. The sawdust is trucked to the mill, where it is dumped into the receiving hopper, passed by conveyor belt under a magnet to remove metals, and onto a hogger where it is ground to a uniform size. The sawdust is then lifted by a bucket elevator to the top of the storage silo, which holds an 8-day supply of fuel.

Sawdust exits the silo from the bottom, where it is collected in a metering bin which dispenses it to a screw conveyor leading to the boiler. The metering bin has sensing devices to monitor the steam pressure in the

boiler and releases sawdust as needed to maintain a constant pressure. The measured charge of sawdust is blown into the dutch oven where combustion takes place. The heat produced by this combustion is introduced into the boiler where the steam is generated.

The exhaust gases pass through a series of cyclone separators to remove any particles and then into a smoke stack. At this point a heat exchanger transfers heat from the exhaust and reinjects it under the grate in the combustion chamber. Since the mill has ample capacity in their dyehouse heat exchanger, they are using the preheated water as their boiler make-up water. This results in greater energy efficiency for the system.

The new boiler system has eliminated the need for 300,000 gal/yr of fuel oil. The sawdust fuel costs approximately \$12.00/tori;; the company reports a 66% savings on fuel costs. They estimate a payback period of only four years for the new system. The new boiler is also a much cleaner system since it is equipped with state-of-the-art pollution control devices. Cyclone separators scrub the vapors and prevent the particulate "fallout" that was present with the oil-fired steam generator.

Another common waste reuse practice is the sale of rags, seam waste, and selvage trimmings, which are sold to craft supply stores and rug manufacturers. Then wastes, especially selvage trimmings from knit goods, can be sold at a profit and the solid waste from such sources is thereby eliminated.

4.2.1 Waste Exchanges [401

One important method of waste reuse involves the use of one industry's waste products as raw material in another manufacturing operation. There are

several agencies and businesses that deal exclusively in the exchange of wastes between industries [49].

There are essentially two types of waste exchanges: passive (information) and active (material). In a passive or information waste exchange, generators list wastes they have available and want to transfer and potential users list wastes they want. This information is listed by code, in a catalog or brochure, where only the waste description, quantity, availability and general location are identified. Companies generally have the option of listing confidentially or nonconfidentially. If the listing is confidential, upon receipt of a letter from a company interested in that waste, the waste exchange notifies the listing firm. Contact with the interested party is then initiated by the listing firm at its own discretion. The inquirer is notified that the lister will contact him. with a nonconfidential listing, the exchange notifies the inquirer and lister of the other's identity. This permits either one to initiate the contact. The exchange does not become involved in the subsequent negotiations between the two parties to complete the transfer of the material. Other functions of information exchanges may include providing up-to-date waste recycling news, along with the listing in their catalogs and making an active effort to find possible users for available wastes.

In an active or materials exchange, a broker serves as a liaison between the generator and potential users of the wastes. They may actually take possession of the wastes and actively participate in the negotiations for a brokerage fee. The materials exchange may analyze and treat the waste to make it a suitable raw material for buyers to use. The type of exchange actively seeks buyers for the wastes.

The Southeast Waste Exchange (SEWE) is a nonprofit information clearing-house located in the Urban Institute of The University of North Carolina at Charlotte. It was established to identify and bring together industrial,waste generators with potential users and companies seeking waste management services with those which can provide them and serves both North and South Carolina.

The SEWE publishes the Waste Watcher, a bimonthly bulletin which includes listings of materials available or wanted and products and services available or wanted. A "Notes" section includes articles on PWE services and activities, current federal, NC and SC legislation on wastes, successful recovery and recycling accounts, upcoming conferences and workshops, and other items of interest.

In a June 1984 report on "Liability Associated with Waste Exchanges," Glenn Dunn, Attorney, North Carolina Solid and Hazardous Waste Management Branch, concluded that, "Finally, it seems clear that disposition through a Waste Exchange will carry lower potential liability to a generator than disposal of waste off-site."

5.0 SUMMARY

This document presents some methods that have been used, or that can be used, to reduce pollution and accomplish cost reduction or economic advantage at the same time. Unfortunately, the material presented here is limited because of two reasons. First, the scope of this document did not permit all possible avenues to be fully explored. Second, almost all types of strategy for source reduction are site-specific. Thus, it is not possible to cover every situation in a generic way. However, it is hoped that the material presented here, along with the references cited, will lead to innovations and ideas which can result in cost savings and source reduction of pollutants in commerce. Additional references are given in bibliographies.

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