

## WATER USES AND WASTES IN THE TEXTILE INDUSTRY

John J. Porter, Donald W. Lyons, and William F. Nolan\*

Approximately 13 trillion gallons of water are discharged by U. S. industry each year. The textile mill products industry discharges about 135 billion gallons or 1% of the total. The relative quantity of water used by the textile industry seems small, but when one considers that the textile industry is concentrated in four or five states in the Southeast on inland water supplies, the water use is quite significant.

Another very important factor to consider is the rate at which this growing waste stream is changing in composition. Due to new products introduced onto the market, a waste stream that may have once been homogeneous and biodegradable can become heterogeneous and inert.

The lint from textile manufacturing and finishing is a noticeable part of the suspended solids in textile waste. In the case of natural fibers, biological degradation will occur when the fiber is retained with the sludge in the treatment plant. However, this is not true for most synthetic fibers which are comparatively inert. The buildup of synthetic fibers in a treatment plant using mechanical aeration can cause damage to pumps and aerators unless special precautions are taken to remove fibers from the waste stream as it enters the plant. Generally, this is done by screening the waste stream as it enters the treatment plant. In some cases, this may be a difficult operation because a screen system fine enough to remove fibers 15  $\mu$  in diameter may easily clog or remove suspended solids that are suitable for biological treatment. Synthetic fibers can amount to 5-10% of the weight of the sludge.

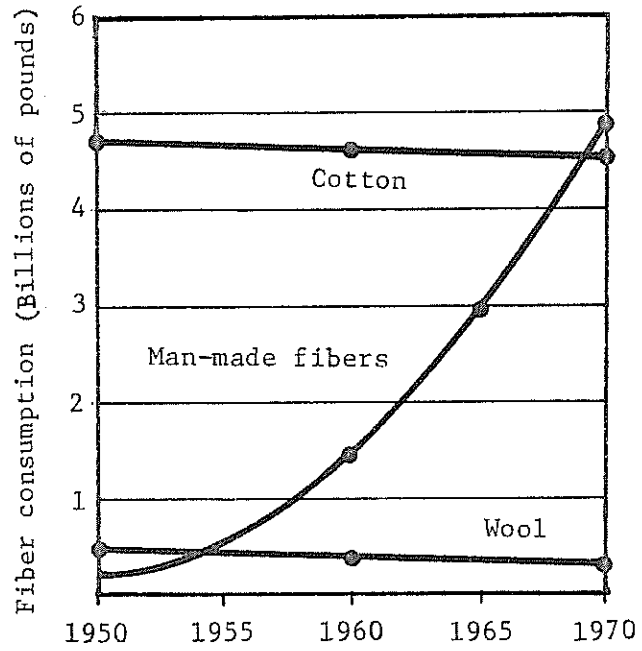
### Effluent Characterization

A number of mechanical operations have to be performed to convert textile fibers into fabrics. The fibers must be combined into yarns and then the yarns into fabrics. After fabrics are manufactured, they are subjected

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The Authors are respectively, Associate Professor of Textile Chemistry; Associate Professor of Textiles and Mechanical Engineering, and Research Advisor for the Textile Institute; Research Assistant, Clemson University, Clemson, South Carolina 29631.

Figure 1. Textile fiber consumption in the U. S.



Source: Textile Organon, 40, 191, 1969.

to several wet processes collectively known as finishing, and it is in these finishing operations that the major waste effluents are produced.

#### Cotton

The consumption of cotton fibers by textile mills in the United States exceeds that of any other single fiber (Figure 1). Slashing is the first process in which liquid treatment is involved. In this process, warm yarns are coated with "sizing" to give them abrasive resistance to withstand the pressures exerted on them during the weaving operation. The principal slashing polymer used before 1960 was starch which was easily degraded biologically and should present no problem to the conventional waste treatment plant other than BOD loading.

Development of many synthetic fibers in the 1950's and their use in blended fabrics created the need for new sizes which were more compatible with the hydrophobic fibers. Some of those which are still in use are polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and polyacrylic acid.

If an average size concentration of 10% is assumed to be present on woven fabrics, which constitute 70% to 80% of the fabrics produced, approximately 400 million lb of size per year are currently entering textile finishing waste streams. Since PVA and CMC are resistant to biological degradation, conventional treatment methods would not be expected to alter their chemical structure. While the polymer may be partially removed from the waste water by adsorption on the sludge, it is quite questionable whether this is an effective method of treatment.

The operation of desizing removes the substance applied to the yarns in the slashing operation, by hydrolyzing the size into a soluble form. There are two methods of desizing--acid desizing and enzyme desizing. In acid desizing, the fabric is soaked in a solution of sulfuric acid, and in enzyme desizing, complex organic compounds produced from natural products or malt extracts are used to solubilize the size. Due to the unstable nature of these organic compounds, the whole bath must be discarded after each batch. Desizing contributes the largest BOD of all cotton finishing processes--about 45%.

Scouring follows desizing. In this process, cotton wax and other non-cellulosic components of the cotton are removed by hot alkaline detergents or soap solutions. In most modern plants, scouring is done in conjunction with desizing rather than as a separate operation. Caustic soda and soda ash

along with soaps and synthetic detergents and inorganic reagents are used to remove the noncellulosic impurities. The waste liquor will have a 0.3% alkaline concentration.

A few of the major chemical manufacturers are now offering solvent processes to the textile industry for scouring where little water is used. In these cases, nonflammable chlorinated solvents are used, and the projected solvent recovery is between 90% and 97%. However, nearly 1 ton of solvent per day per range will reach the atmosphere or waste stream.

Bleaching, the next process, removes the natural yellowish coloring of the cotton fiber and renders it white. The three bleaches most commonly used for cotton are sodium hypochlorite, hydrogen peroxide, and sodium chlorite. The bleaching process contributes the lowest BOD for cotton finishing.

Mercerization gives increased luster to cotton fabrics, but more importantly, imparts increased dye affinity and tensile strength to the fabric. The process uses sodium hydroxide, water, and an acid wash. The effluent from the overall process has a high pH and also a high alkalinity if the caustic material is not recovered. After mercerizing, the goods are sent to the dye house or color shop. The dyeing process is carried out in an aqueous bath with pH variations of 4 to 12.

In the color shop, the goods are printed with colored designs or patterns. The color is imparted to the fabric from rolling machines which contain the printing paste. This paste contains dye, thickener, hygroscopic substances, dyeing assistants, water, and other chemicals. The pollution load from the color shop comes mainly from the wash-down rinses (used to clean the equipment in the shop) and the cloth rinsings and is rather low in both volume and BOD. When a mill does both printing and dyeing, the BOD contribution of the combined processes is 17%, and the total BOD load comes from the process chemicals used.

Dyes have to be more and more resistant to ozone, nitric oxides, light, hydrolysis, and other degradative environments to capture a valuable portion of the commercial market. It is not surprising, therefore, that studies on the biological degradation of dyestuffs yield negative results when dyes are designed to resist this type of treatment. The range of pollution loads of the various cotton textile wet-processing operations are listed in Table 1.

Federal Water Pollution Control Administration estimates for BOD, suspended solids, total dissolved solids, and volume of waste water for 1970-82

Table I. Pollution effects of cotton processing wastes

Process	Wastes, ppm		
	pH	BOD	Total solids
Slashing, sizing yarn	7.0-9.5	620-2,500	8,500-22,600
Desizing		1,700-5,200	16,000-32,000
Keiring	10-12	680-2,900	7,600-17,400
Scouring		50-110	
Bleaching (range)	8.5-9.5	90-1,700	2,300-14,400
Mercerizing	5.5-9.5	45-65	600-1,900
Dyeing:			
Aniline Black		40-55	600-1,200
Basic	6.0-7.5	100-200	500-800
Developed Colors	5-10	75-200	2,900-8,200
Direct	6.5-7.6	220-600	2,200-14,000
Naphthol	5-10	15-675	4,500-10,700
Sulfur	8-10	11-1,800	4,200-14,100
Vats	5-10	125-1,500	1,700-7,400

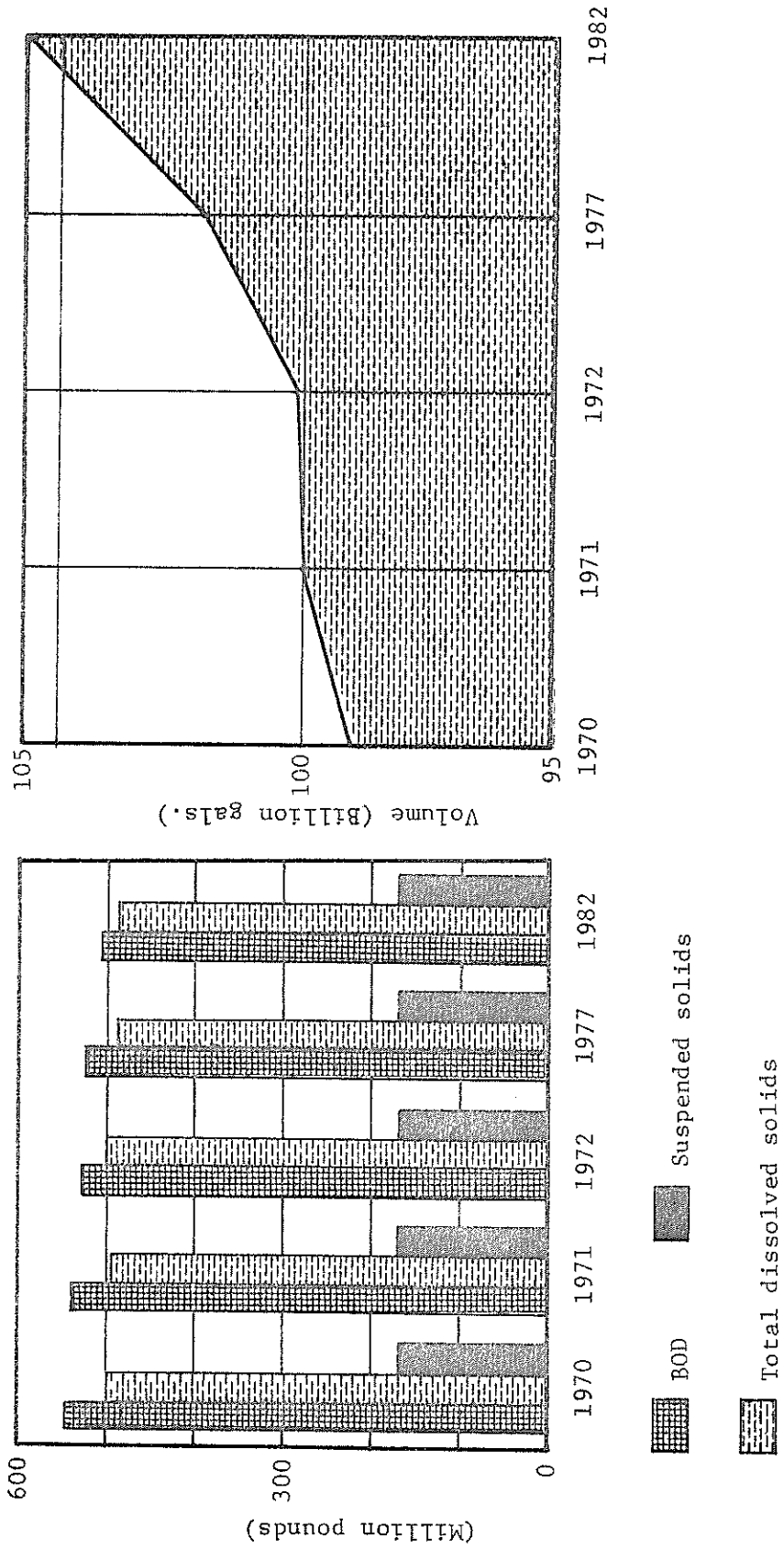


Figure 2. Projected wasteload for cotton finishing wastes.

are shown in Figure 2. The gradual decrease of the gross pollution load in coming years is based on these assumptions: new machinery, which tends to produce less pollution per unit of cloth due to water reuse and countercurrent flow designs; trends in process modification, new chemical manufacture, and better housekeeping will continue; a larger percentage of the wastes will be treated due to increased efficiency of treatment facilities; and increased state, local, and federal pressure.

#### Wool

Wool fiber consumption is the smallest of the three groups, and the trend seems to be toward less demand in the future on a percentage basis. Scouring is the first wet process that wool fibers receive. This process removes all the natural and acquired impurities from the woolen fibers. For every pound of scoured woolen fiber, 1-1/2 lb of waste impurities are produced; in other words wool scouring produces one of the strongest industrial wastes in terms of BOD by contributing 55-75% of the total BOD load in wool finishing.

Depending on whether the fabric is classified as woolen or worsted, the remaining wet processes will vary. Burr picking and carbonizing are steps to remove any vegetable matter remaining in the wool after scouring and before dyeing.

The volume of waste water generated by dyeing, either stock or piece goods, is large and highly colored, and many of the chemicals used are toxic. The BOD load is contributed by the process chemicals used, and represents 1-5% of the mill's total BOD load. Although the following mixing and oiling step does not contribute directly to the waste water volume, the oil finds its way into the waste stream through washing. The percentage contribution to total BOD load of this process varies with the type of oil used.

Fulling or felting is another operation that does not directly contribute to the waste stream, until the process of chemicals are washed out of the fabric. It is estimated that 10-25% of the fulling cloth's weight is composed of process chemicals that will be washed out in this process and discarded.

Wool washing after fulling is the second largest source of BOD, contributing 20-35% of the total. This process consumes 40,000-100,000 gallons of water for each 1,000 lb of wool fabric, and analyses show that wool, once thoroughly washed, will produce little or no BOD on being rewashed. Carbonizing the fabric or stock of fibers (with strong acid to remove cellulose

Table II. Pollution loads of wool wet processes

Process	pH	BOD, ppm	Total solids, ppm
Scouring	9.0-10.4	30,000-40,000	1,129-64,448
Dyeing	4.8-8.0	380-2,200	3,855-8,315
Washing	7.3-10.3	4,000-11,455	4,830-19,267
Neutralizing	1.9-9.0	28	1,241-4,830
Bleaching	6.0	390	908



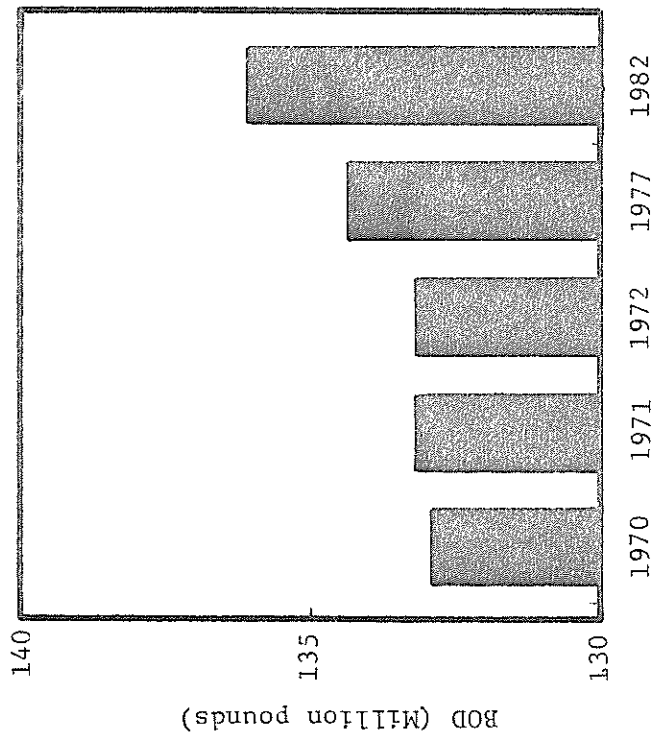
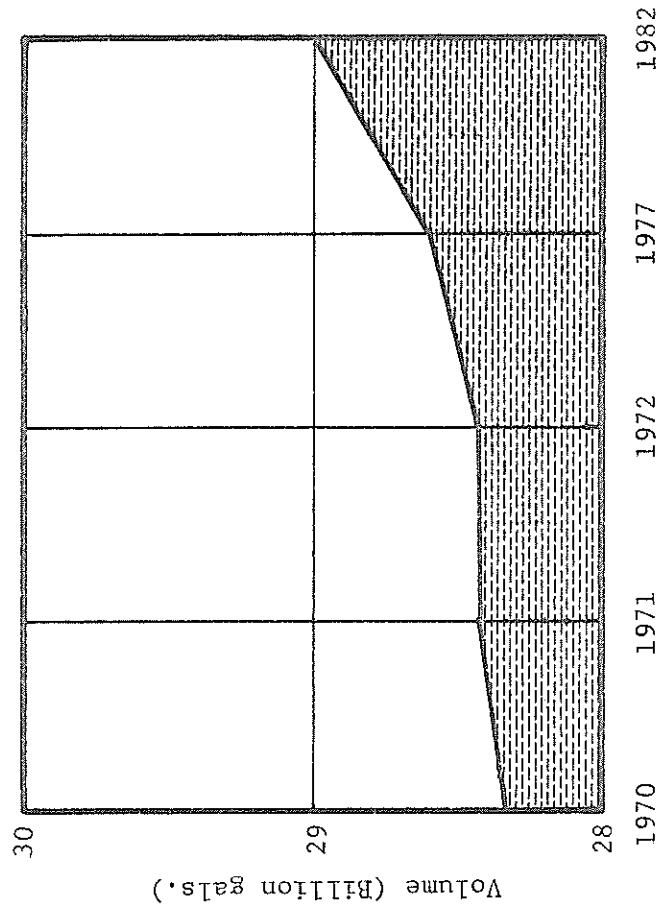


Figure 3. Projected wasteload for woolen finishing wastes.

impurities followed by a soda ash wash) contributes less than 1% of the total BOD load.

Wool is bleached if white fabric or very light shades of colored cloth are required; however, the amount of wool fabric bleached is rather small. With hydrogen peroxide and sulfur dioxide, bleaching the BOD contribution is usually less than 0.5%, and optical brighteners, which use organic compounds, contribute about 1% of the total BOD. In processing woolen fibers, five sources of pollution load exist--scouring, dyeing, washing after fulling, neutralizing after carbonizing, and bleaching with optical brighteners. The average values of the pollution load of each of these processes is shown in Table II. The waste water volume for woolen finishing wastes is shown in Figure 3.

### Synthetics

This category of textile fibers has two broad classifications: cellulosic and noncellulosic fibers. The two major cellulosic fibers are rayon and cellulose acetate; the major noncellulosic fibers are nylon, polyester, acrylics, and modacrylics. Different processes to produce synthetic fibers result in varying pollution loads (Table III).

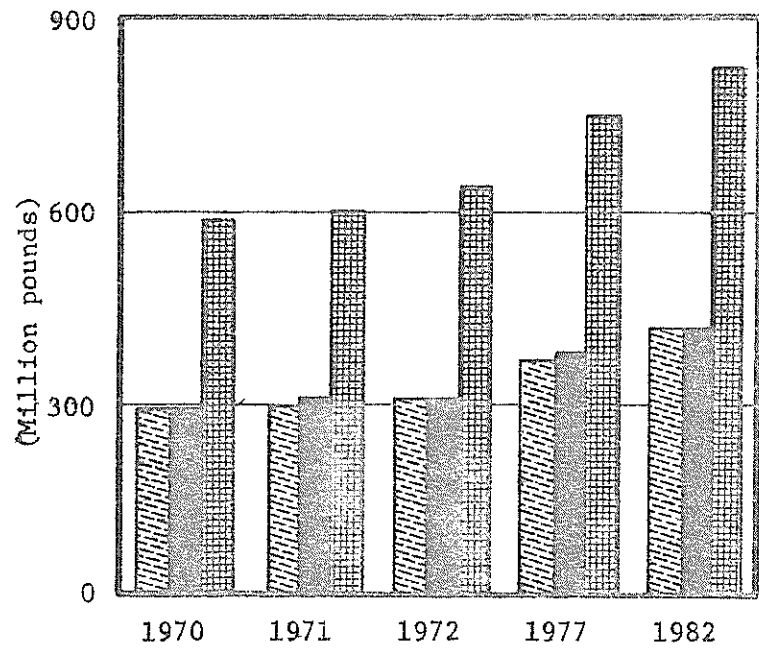
The first process in which synthetic fibers are subjected to an aqueous treatment is stock dyeing (unless the fabric is to be piece dyed). When stock dyeing is used, the liquid waste discharge will vary from about 8 to 15 times the weight of the fibers dyed. Due to the low-moisture regain of the synthetic fiber, static electricity is a problem during processing. To minimize this problem, antistatic oils (polyvinyl alcohol, styrene-based resins, polyaklylene glycols, gelatin, polyacrylic acid, and polyvinyl acetate) are applied to the yarns and become a source of water pollution when they are removed from the fabrics during scouring.




Since the manufacture of synthetic fibers can be well controlled, chemical impurities are relatively absent in these fibers; and if synthetics are bleached, the process is not normally a source of organic or suspended solids pollution.

In finishing rayon, one of the synthetic fibers, scouring and dyeing are usually done concurrently in a single bath. If scouring and dyeing are the only finishing processes given rayon fabrics, an equalized effluent of 1445 ppm BOD and 2000-6000 ppm salt contained in approximately 5000 gallons of water for each 1000 lb of fabric processed will be produced.

Table III. Pollution load of synthetic wet fiber processes

Process	Fiber	pH	BOD, ppm	Total solids, ppm
Scour	Nylon	10.4	1360	1882
	Acrylic/modacrylic	9.7	2190	1874
	Polyester		500-800	
Scour & Dye	Rayon	8.5	2832	3334
	Acetate	9.3	2000	1778
Dye	Nylon	8.4	368	641
	Acrylic/modacrylic	1.5-3.7	175-2000	833-1968
	Polyester		480-27,000	
Salt Bath	Rayon	5.8	58	4890
Final Scour	Acrylic/modacrylic	7.1	668	1191
	Polyester		650	



 BOD     
  Suspended Solids  
 Total Dissolved Solids

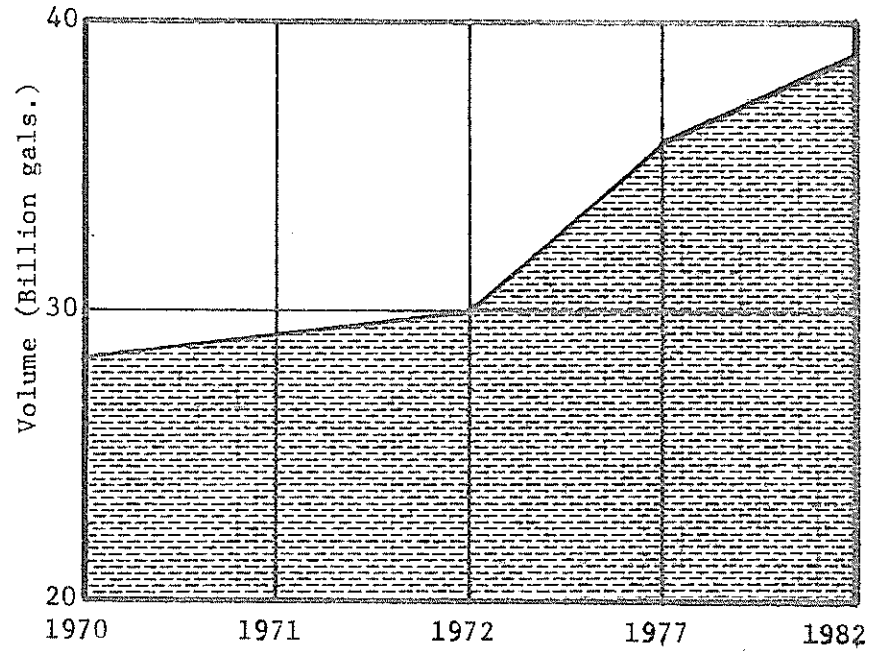


Figure 4. Projected wasteload for synthetic fiber finishing .

For acetate fibers, the wastes from scour and dye baths average 2000 ppm and 50 lb of BOD for each 1000 lb of acetate fabric. Typically, the bath contains antistatic lubricant desizing wastes, which contributes 40-50% of the BOD load; the sulfonated oil swelling agent, which accounts for 30-40% of the BOD load; the aliphatic ester swelling agent, which amounts to 10-20% of the BOD discharged; and the softener which has negligible BOD content.

These processes produce a composite waste of 666 ppm of BOD for each 1000 lb processed; the volume of water required to treat this amount of cloth averages 9000 gallons. If bleaching is substituted for dyeing, the BOD of the discharge of the scouring and bleaching bath is approximately 750 ppm.

Nylon differs from other synthetics in that approximately 1% of the fiber dissolves when scoured. Soap and soda ash are used in the scouring process which averages 1360 ppm and 34 lb of BOD for each 1000 lb of cloth processed. The substances present in the bath contribute the following percentages to the total BOD of the bath; antistatic-sizing compound (40-50%), soap (40-50%), and fatty esters (10-20%).

When nylon is dyed, sulfonated oils are used as dye dispersants. These dye dispersants contribute practically all of the process's BOD, which amounts to an average of 600 ppm and 15 lb for each 1000 lb of cloth dyed. However, the BOD contribution of scouring is roughly 80%, the remaining BOD being contributed by the dyeing process.

Another group of synthetic fibers are the polyesters whose scour wastes average 500-800 ppm of BOD. Processing 1000 lb of polyester fabric will produce 15.5 lb of BOD of which 90% is contributed by antistatic compounds used for lubrication sizing. Because of the high concentrations at which they are used and the inherent high rate of BOD, the emulsifying and dissolving agents used in polyester dyeing will produce high BOD loads. The rinses in polyester finishing are usually low in BOD. But, the processing of polyester uses an average of 15,000 gallons of water per 1000 lb of fiber. Projected gross wasteload for synthetic fiber finishing is shown in Figure 4.

#### Acrylics and Modacrylics

Although these two fiber types have different physical and chemical properties, they are both subject to the same finishing techniques. The waste from the first scour averages 2190 ppm and 660 lb of BOD per 1000 lb of processed fiber. The chemical components of the bath are the antistatic compound, which accounts for 30-50% of the BOD, and the soaps used to accom-

plish this process. When using acid dyes, the dye baths average 175 ppm and 5.3 lb of BOD per 1000 lb of fabric, the total BOD load coming from the dye carriers.

The final scour averages 668 ppm and 20 lb of BOD for 1000 lb of cloth. This final scour is accomplished with synthetic detergents and pine oil, which together contribute practically all the BOD. The equalized discharges will have a BOD of 575 ppm and 120.9 lb in a volume of 25,000 gallons of wastewater for each 1000 lb of acrylic and modacrylic fabric processed.

#### Finishing

A treatment of a fabric that modifies its physical or chemical properties may be classified as finishing. Examples include permanent press finishes, oil repellents, soil release agents, low-crock polymers, abrasion-resistant polymers, fire retardants, lamination polymers, germicide and fungicide chemicals, to mention a few. A small number of these materials are biodegradable; however, most are not.

The polymers used for textile finishing are generally supplied to the finishing plant as emulsions which are sensitive to pH, salt, or agitation and may coagulate when they enter waste streams. Sewer lines may then become clogged with inert materials which have to be removed by hand. Although the bulk of the polymer emulsion can be coagulated and removed in a treatment plant, some of it remains emulsified and is not removed by biological treatment. For complete removal of the polymer emulsion, chemical treatment is sometimes necessary. However, this is an additional step which in itself could replace much of the need for biological treatment.

Most of the finishes used for wash and wear and permanent press fabrics are manufactured from urea, formaldehyde, melamine, and gloxal compounds. Some of these products are readily degradable by microbial action; others are not. The formaldehyde derivatives can react with themselves or other chemicals in the waste stream to form insoluble products that may be removed by sedimentation.

A class of finishing chemical that has come into prominence in recent years is fire retardants. Most of the commercial fire-retardant finishes are phosphorus- and nitrogen-containing compounds. One such compound, tri-aziridyl phosphine oxide (APO), could present a serious problem if it got into a natural stream. The chemical inactivity of APO would facilitate its hydrolysis in a waste stream and prevent the parent compound from reaching

the discharge water of a treatment plant. Whether or not these initial hydrolysis products are toxic or harmful is not known. This points to the increasing need for the characterization of industrial waste.

In the future, waste streams from different processing operations will have to be isolated and treated by either chemical or biological methods. The choice of treatment will naturally depend on the composition of the stream. By using this approach, industry will have more latitude in choosing chemicals and processes for their inherent production advantages and not their effect on pollution.