Water, Energy And Chemical Recovery From Desizing

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□ Approximately 400 million pounds of sizing chemicals per year enter textile finishing waste streams from the desizing operation. These size chemicals, which are applied to warp yarns to protect them during the weaving operation, represent a valuable material which may be recovered and then reused in the slashing operation.

Using as an estimate 1 percent size concentration in desizing waste water, the amount of water used for desizing approaches 5 billion gallons per year. Assum-

Fig. 1. Flow diagram for desize section of evaluated preparation range.

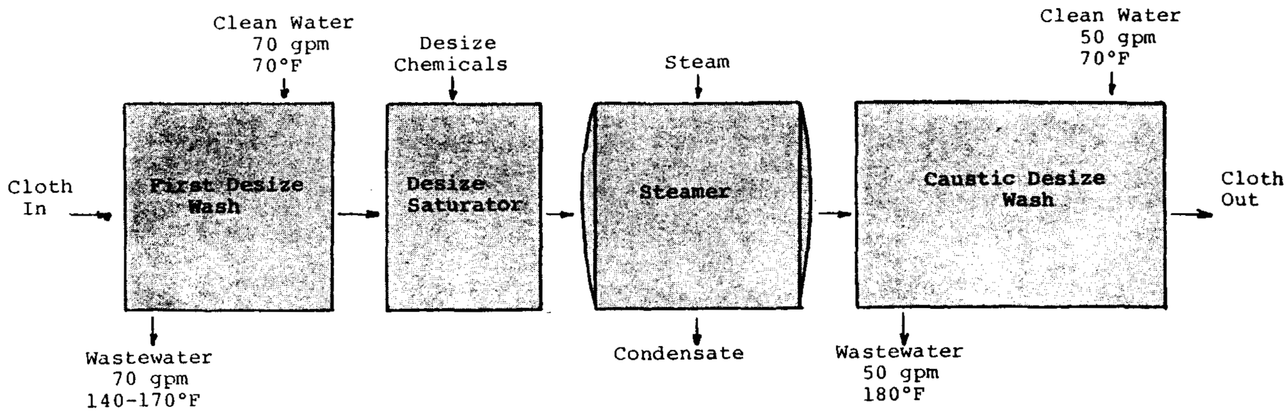

Table I: Extraction of grey fabric samples using boiling deionized water and detergent.

Sample identification	Weight loss of fabric Test 1	Test 2
30 sec boil	9.28	8.78
1 min boil	9.66	9.00
2 min boil	9.38	9.06
5 min boil	9.52	8.82

Table II: Comparison of total wax, PVA, and CMC removed from fabric.

	Total wax removed (%)	Total PVA and CMC removed (%)
Removed in first desize wash	12.3	57.5
Removed in caustic desize wash	24.6	39.3
Total removed	36.9	96.8

ing that the average temperature is 180°F, the energy value for the desize waste water is approximately 5 x 10^{12} Btus per year. At $2 per million Btus, the energy value alone represents a cost of more than $10 million per year to the textile industry. This value would double if the size concentration was 0.5% in waste water, as is thought to be the case in many mills.

Comparison of starch and synthetic sizes

The principal slashing polymers used today are starch, polyvinyl alcohol (PVA), and carboxymethyl cellulose (CMC). Starch and the synthetic polymers meet the general criteria for cotton and cotton/polyester blend warp sizing, but starch is the most abundant, has the lowest cost and, therefore, is the most widely used.

Desizing of slashing polymers contributes the largest Biochemical Oxygen Demand (BOD) of all cotton finishing processes—about 45 percent.[1] This proportionally large amount is due mainly to the high oxygen demand of the starch present in size formulations.

Starch, a natural polymer of glucose, is highly biologically degradable. Biological oxidation of the starch begins immediately upon entering the waste stream, proceeds rapidly for three days, and will consume almost a pound of oxygen per pound of starch.[2] Since most textile mill waste streams are treated using conventional biological methods, the treatment plants need sufficient volume capacity for retention and oxidation of the starch waste.

Because of the possibility of recovery and the relatively large contribution which starch desizing wastes make to the biological treatment of textile mill effluents, some mills are switching completely to the synthetic polymers or to combinations of starch and synthetics. These synthetic sizes are much more resistant to biological degradation and so have comparatively low BOD values.

Federal legislation calls for zero discharge of pollutants in 1985. To meet this goal, an effective method for removal of synthetic sizes is needed. Physical and chemical treatment methods have been used, but neither has been found to be satisfactory.[3]

A method is needed which will decrease significantly not only the BOD load but also the refractory soluble synthetic size wastes from desizing operations. Two methods are open to textile mills:

☐ Recovering the size from the waste stream for reuse.

Table III. Results of membrane separation treatment of samples of first desize rinse water. Union Carbide 3NJR type membranes were used.

Parameter[a]	First desize rinse water: Raw feed	Final concentrate	Composite product	Final product	Percent removed from raw feed[b]
COD	3660	24,550	610	715	83.3
TOC	1985	14,390	330	550	83.4
pH	6.2	5.6	6.7	7.15	—
Solids					
Total	2735	16,845	810	925	70.4
Suspended	82	845	<1	<1	>99
Volatile	2430	15,645	570	605	76.5
Color	1135	4,725	290	520	74.4
Conductivity	550[c]	1,100[c]	535[c]	345[c]	—
Surfactants	0.02	—	—	—	—
Oil and grease	33	—	2.1	2.9	93.6
Metals					
Chromium	<0.003	1.4	0.01	0.05	—
Copper	0.02	1.5	0.05	0.09	75.0

[a] All parameters have units of mg/1 except pH (unitless), color (Pt-Co units), and conductivity (μmho/cm).

[b] As determined from composite product results.

[c] Rechecked.

☐ Developing more rapid treatment methods.

Of the two, the first is the more desirable. Both methods will incur additional capital and operating costs, but only the first provides a payback capability. If size chemicals are used which can be applied and recovered, the size load on the waste streams would be eliminated, meeting all legislative standards. In addition, savings can be claimed by the substantial reduction of chemicals used.

Starch must undergo degradation, usually by enzyme treatment, before it is removed from the fiber. Starch is also an unstable compound in a waste stream due to its biodegradability. It would appear that recovery of starch would be difficult due to its rapid degradability.

The synthetic sizes have the advantage of being water soluble both when used alone, and in combinations with starch. They can be removed using hot water, making it unnecessary to use special desize chemicals. The synthetic sizes also have thermal stability and resist biodegradation, both factors supporting the recovery concept.

Method for recovery

Due to their stability, the long chain molecules of synthetic sizes are recoverable using membrane separation technology, which includes reverse osmosis and ultrafiltration. Ultrafiltration is the more suitable and economical recovery method because of the desire to recover the massive polymeric size freed of salt impurities present in the waste water.

The ultrafiltration semipermeable membrane holds back polymer while water passes through. The concentrated size is then stored for reapplication on the slasher, and the filtered hot water is returned to the desizing process to wash out more size.

The energy content of waste water was once thought to be a problem that interfered with the treatment of the waste stream. Now it is considered valuable and can be recovered as usable hot water by this membrane separation technique. The recovered hot water used in the desizing operation has an energy value of near $3/1000 gallons and a water and waste treatment savings of $1/1000 gallons.

To be most effective the ultrafiltration system is applied directly to the desize waste water before any mix-

Table IV: Results of membrane separation treatment of samples of caustic desize wash water. Union Carbide 3NJR type membranes were used.

Parameter[a]	Caustic desize wash water Raw feed	Composite product	Final concentrate	Percent removed from raw feed[b]
COD	21,250	3,310	132,700	84.4
TOC	11,530	1,920	57,810	83.3
pH	12.05	12.0	11.6	–
Solids				
Total	16,360	5,330	90,990	67.4
Suspended	575	<1	400	>99.8
Volatile	12,880	3,280	80,000	74.5
Color	2,290	190	12,040	91.7
Conductivity	4,800[c]	8,000[c]	6,500[c]	–
Surfactants	0.04	–	–	–
Oil and grease	18	–	–	–
Metals				
Chromium	<0.013	0.178	2.7	–
Copper	0.335	0.388	1.6	–

[a]All parameters have units of mg/1 except pH (unitless), color (Pt-Co units), and conductivity (μmho/cm).

[b]As determined from Composite Product results.

[c]Rechecked.

ing with other process effluent occurs. When this is done, the size, the water, and some energy all can be recovered with minimal effluent waste load.

The ultrafiltration system has successfully been applied in recovering PVA size in a plant.[3] Besides energy, chemical, and water savings and reduced pollution load, some of the other benefits found for the actual application of the system are:

☐ Possible payout in 18 months is obtained due to the recovery of 85 to 90% of PVA.

☐ Reliability as shown by four years of continuous service with no major system failures.

Table V. Results of membrane separation treatment of samples of neutralized desize wash water. Union Carbide 3NJR type membranes were used.

	Neutralized desize wash water				
Parameter[a]	Treated feed (neutralized desize wash water)	Composite product	Final product	Final concen-trate	Percent removed from treated feed[b]
COD	22,790	1490	1575	48,800	93.5
TOC	10,500	785	785	17,910	92.5
pH	9.4	8.25	8.7	7.5	—
Solids					
Total	18,580	5235	5710	34,300	71.8
Suspended	550	30	42	820	94.5
Volatile	15,900	2310	3360	30,650	85.5
Color	2,725	480	425	3,500	82.4
Conductivity	5,700	5200	5800	5,500	8.8
Surfactants	0.13	—	—	—	—
Oil and grease	61	21	35	5	65.6
Metals					
Chromium	<0.007	0.009	0.033	0.20	—
Copper	0.40	0.30	0.27	0.87	25.0

[a]All parameters have units of mg/1 except pH (unitless), color (Pt-Co units), and conductivity (μmho/cm).
[b]As determined from Composite Product results.

☐ No quality problems. Excellent dyeings are obtained with material sized with recovered PVA.

☐ A more consistent size is obtained resulting in improved loom performance.

Investigations of size removal and recovery

Investigations of size recovery have been made at Clemson University under a contract supported by the Environmental Protection Agency (EPA).[4] Fabric and waste water samples from a continuous preparation range were analyzed to determine the most practical and advantageous method of recovering the size chemicals (PVA, CMC, and sizing wax) from a 65/35 polyester/cotton blend.

The grey fabric entered the preparation range, was heat set, and then passed into the first desize wash, operating at 140° to 170°F, then into a caustic desize saturator, a steamer, and a caustic desize washer. From there it was scoured and bleached. A flow diagram for the desize section of the range is shown in Fig. 1.

Since the material balance and efficiency of the washing process is important to the recovery cost, fabric and waste water samples were taken at various points along the desize section of the range. Gravimetric and spectrophotometric techniques were used to analyze the fabric and waste water to obtain a qualitative and quantitative measure of the sizing chemicals present. A spot test was used to detect the presence of PVA on fabric samples.

In an attempt to completely remove wax, PVA, and CMC from the fabric, grey fabric samples weighing 15 grams were boiled for 15 minutes in 800 ml of deionized water containing 2 ml of detergent. Analyses confirmed that about 9 percent of the grey fabric weight was composed of sizing chemicals which were removed by the boiling water.

To determine the length of time necessary completely to remove the sizing chemicals, grey fabric samples were boiled in deionized water and detergent for periods of time ranging from 30 seconds to 5 minutes. As may be seen in Table I, a boiling period of 30 seconds to one minute is apparently sufficient to remove the size.

Extractions of fabric samples using various solvents were also conducted to evaluate methods of quantitative determination of wax on the fabric. Mild extractions with solvents such as DuPont Freon® (1,1,2-trichloro-trifluoro-ethane) and benzene were found to remove approximately the same amount of wax. A much harsher extraction using a Soxhlet extractor was found to remove both natural and synthetic oils and waxes from the polyester-cotton fabric.

Concerning experimental methods, the determinations of percent weight loss of fabric by extraction were more consistent and more accurate when residue weights were used rather than actual weighings of the fabric before and after extraction.

Mild Freon extractions followed by boiling water extractions were conducted on grey fabric samples, fabric samples after the first desize washing, and fabric samples after caustic desize washing. The results, as given in Table II, show that 57.5 percent of the total PVA and CMC size is removed in the first desize wash and 39.3 percent is removed in the caustic desize wash. Only 12.3 percent of the sizing wax was removed in the first desize wash and 24.6 percent was removed in the caustic desize washers.

Infrared spectra of the fabric extracts and waste water residues were obtained and compared with spectra of the three major constituents used in the size formulation. Comparisons proved that these three chemicals constituted more than 95 percent of the material washed from the fabric and present in the waste water.

When the fabric and waste water samples were taken from the preparation range, large, 100 gallon samples of the waste streams were collected so membrane separation tests could be conducted at Clemson University to determine the possibility of recovering sizing chemicals from the waste water.

The membrane separation tests were conducted using an ultrafiltration membrane on carbon support tubes supplied by Union Carbide on samples taken from the first desize wash and the caustic desize wash. The

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Record foundation grant goes to help NCSU textile studies

The North Carolina Textile Foundation will contribute a record $196,000 in student scholarships, supplements to faculty salaries and other aid to the School of Textiles at North Carolina State University during the current school year.

The $4 million foundation, a non-profit organization of textile related companies, has contributed more than $3 million to the textile school since the foundation was organized in 1942.

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results of the tests for the first desize wash are presented in Table III. Around 83 percent of the COD and TOC, 70 percent of the total solids, and 74 percent of the color in the samples were removed by the ultrafiltration treatment. These results were determined by comparison of concentrations in the waste water samples to concentrations in the product water samples.

Table IV presents the results of membrane separation treatment of the caustic desize wash water samples. In this case 83-84 percent of COD and TOC, 67.4 percent of total solids, and 97 percent of color were removed.

A portion of the samples of the caustic desize wash water were neutralized to a pH of 7 and treated by membrane separation. The results of this treatment are shown in Table V. Apparently neutralization aided in the removal of COD and TOC. In this case 93.5 percent of the COD and 92.5 percent of TOC were removed.

For membrane recovery to be economical, efficient size removal must be obtained. To obtain a more efficient desize system, certain process requirements are necessary. These are:

- ☐ Removal of recoverable size needs to be as high as possible with a minimum water usage. For example, PVA desize effluent should be at a concentration of from 1 to 1.5 percent. Reducing the hydraulic load to the membrane separation unit or to any waste water treatment facility will allow the use of smaller units requiring less capital and operating cost.
- ☐ Heatsetting has been shown to adversely affect the removal of size. For example, PVA becomes very difficult to remove when the sized fabric has been heat-set at above 150°C. As heatset temperatures above 150°C are increased, the efficiency of removal declines sharply.[5]
- ☐ Efficiency of synthetic size removal increases with increasing wash temperature. PVA, for example, is most effectively removed at temperatures above 75°C.[5]
- ☐ Better desizing results are obtained if grey sized fabric is initially saturated with a desize solution (detergent), followed by a residence time in a steamer or J-box. This allows the size to be more easily solubilized.

Using these precautions, only one wash system should be needed with a maximum size removal being obtained.

Conclusions

Experiments and data from actual applications have proved that size compositions of synthetic, recoverable sizes can be formulated to meet fully the requirement of efficient weaving for cotton yarns, and blends. Although more expensive than starch, the economic advantages of using the synthetic polymers more than outweigh the higher initial cost. Some of these economic advantages include:

- ☐ Easier removability which greatly reduces the need for desize chemicals.
- ☐ Overall reduction in size cost due to stability and recoverability of synthetic sizes.
- ☐ Enhancement of treatability of composite wastes relieved of the high BOD chemicals, high refractory chemicals, and high temperature water normally incurred with desize waste water.
- ☐ Energy recovery by direct recycle of hot water.
- ☐ Reduction in water cost.

By making process and chemical modifications in the slashing and desizing operations using the concept of conservation and recovery, the whole picture of waste treatment can be changed from a requirement of a regulatory agency to a profitable endeavor. ☐☐☐

Bibliography

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