A Demonstration of Reuse of Spent Dyebath Water Following Color Removal with Ozone

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ABSTRACT

Results of a project to evaluate the technical and economic feasibility of renovating spent reactive dyebath wastewater with ozone has been reported. A pilot scale study of dyebath reuse was conducted using ten commercial dye shades. Dyeings were performed in a tumbler type dye machine equipped to automatically collect the spent dyebath. Color reproducibility of the dark shades was good in water in which 50-90% of color was removed by ozonation. Dyeings of pastel colors and very bright shades required 95% or greater color removal for good shade reproduction. Ozonation was done in a continuous ozone contactor with ozone generated from oxygen. The effects of temperature and pH on decolorization of spent dyebath water with ozone were studied. Kinetics of color removal by ozone were studied. Ozone requirements to decolorize spent reactive dyebath water were measured. Decolorization of spent reactive dyebath water using ultraviolet light and hydrogen peroxide was also studied briefly.

KEY TERMS

Hydrogen Peroxide
Ozonation
Ultraviolet Light
Wastewater

Elimination of color from textile wastewater is of both immediate and long term interest to textile manufacturers. Textile manufacturers in Alabama and other southeastern states either currently or will in the future have to limit the discharge of color from their plants. The ability to economically eliminate or lower the color in textile wastewater will have a major influence on the continued viability of many textile manufacturing plants. Historically, most textile plants have favored treating wastewater after it leaves the plant rather than eliminating pollutants at their source in the manufacturing process.

The treatment of waste leaving the plant represents an additional cost in manufacturing a product. Even though the concentration of color in wastewater may be very low, the color may still be visually objectionable. Color in textile wastewater is not very concentrated because it has been diluted by other process wastewaters. Color is a special problem in waste treatment because biological waste treatment systems do not remove color well. Technology is needed for removal of color at its source (dyeing processes) before it has been diluted by wastewater from other parts of the textile manufacturing plant. Elimination of color from dyebath water after dyeing may make the water suitable for reuse in the dyeing process or in some other process in the manufacturing plant. Dyebath wastewater also contains valuable chemicals and heat which can possibly be recycled if the color in the water is destroyed.

The objective of this project was to evaluate the technical and economic feasibility of renovating spent reactive dyebath wastewater with ozone. A reactive dye/cotton dyeing system was chosen for the study because reactive dyes fix only partially to cotton. As much as 50% of dye from the process remains unfixed, thus creating a major source of color pollution. Furthermore, dyeing with reactive dyes requires the addition of enormous quantities of salt (sodium chloride or sodium sulfate) to the dyebath. The salt enters the wastewater from the plant and becomes a major contributor to aquatic toxicity of textile wastewater.

Literature Review

Textile companies and researchers have studied the feasibility of dyebath reuse for many years and dyebath reuse has been demonstrated and used commercially. In the mid- 1970s, Textile Systems Inc. (TSI) installed dyebath reuse processes in four textile mills in the United States. Two of these were carpet plants dyeing nylon with acid dyes, one was a polyester knit piece dyeing plant in Florida using disperse dyes, and one was a knit fabric dyehouse in North Carolina dyeing polyester/cotton blends with direct and disperse dyes. The process installed at these four plants used chlorine to decolorize residual dye in the spent dyebath and reused the water to rinse and dye fabrics.[1,2] The water was dechlorinated with sulfur dioxide after chlorination and before the water was reused in dyeing. The process was reported to produce successful dyeings and significant cost savings. The payback period based on chemical and energy savings was reported to be six months to two years.

In 1980, Auburn University reported the results of laboratory scale studies concerning the TSI chlorination system.[3,4] Russell Corp. sponsored Auburn's studies which used formulations and procedures based on actual mill practices. In addition to chlorination, Auburn studied ozonation for color removal from spent dyebath water. A total of 28 dyes was included in the studies. Chlorine rapidly decolorized acid and reactive dyes but partially decolorized direct and disperse dyes at a slower rate. Even large doses of chlorine failed to completely decolorize direct and disperse dyes. Direct and disperse dyes formed persistent yellow decomposition products. Chlorine was reported to be more effective for dye decolorization at pH 3.5 than pH 7.0 or 10.0. Ozone decolorized dyes quicker than chlorine and rapidly decolorized all dyes studied except the disperse dyes. The disperse dyes were eventually decolorized by ozone, but the reaction rate was slower than with the water soluble dyes. Various substances interfered with color removal by ozone and chlorine. Enzyme-degraded starch and sodium nitrite were reported to interfere with the decolorization reactions of dyes with either chlorine or ozone.

The Russell-sponsored Auburn University project also included studies on dyebath reuse with direct, reactive, acid and disperse dyes following chlorination and dechlorination of the spent dyebath water. Repeated dyeings of polyester with disperse dyes, nylon with acid dyes and cotton with reactive dyes were successfully demonstrated in the laboratory. Dyeings of cotton with direct dyes in chlorinated water were unsuccessful. The difficulties with direct dyes were attributed to inadequate control of salt concentration in the recycled water and interference of sodium nitrite (from developed dyeing) with decolorization of the dyes by chlorine. Although the process was deemed technically and economically feasible for many applications, it was not implemented because of unfavorable economics of retrofitting the existing dyehouse for dyebath reuse.

In 1992, the National Textile Center sponsored a study of reuse of vinyl sulfone and vinyl sulfone/monochlorotriazine mixed bifunctional reactive dyes on cotton.[5] The process used ozone to decolorize mixed spent dyebath water from three single component dyeings (red, yellow and blue) and recycled the treated water in repeated dyeings of the same three shades. The dyeings were reproducible through the five recycles attempted with both types of reactive dyes. A coarse filtration step was required with the vinyl sulfone dyes prior to ozonation to remove insoluble colored particles. In the absence of the filtration step, slightly lower brightness was obtained in the yellow shade in recycled water compared to the control dyed in fresh water.

The Georgia Institute of Technology published a series of papers beginning in the late 1970s concerning direct reuse of dyebaths. The process they used was only applicable to the dye classes in which the dye molecule is not chemically changed during the dyeing process. The process consisted of spectrophotometrically measuring the quantities of residual dyes in spent dyebaths and reconstituting the baths to the dye concentrations required in the next dyeing. Dye classes in which the dye molecules are not chemically altered during the dyeing process are acid dyes, disperse dyes and direct dyes. Reactive and azoic dyes undergo chemical modifications in the dyeing process which would make them unsuitable for reuse by this direct measurement and reconstitution method. The process was demonstrated in a commercial setting using acid dyes on nylon hosiery. An average of 30 batches of hosiery were dyed in the same dyebath. Substantial savings were reported in dye usage, chemical auxiliaries, water/sewer costs and energy.[6-8] The process was also demonstrated in a laboratory jet dyeing machine with disperse dyes on polyester knit fabric.[9] The spectrophotometric analysis method used Beer's Law which is not valid for the disperse dye in the residual bath. To overcome this limitation, the dye in a sample of the spent dyebath was extracted into toluene to make a solution which could be analyzed spectrophotometrically.

Dyebath reuse using the measure and reconstitute method was studied in the laboratory at the University of Rhode Island with direct dyes on cotton.[10] The study used selected direct dyes that are known to be capable of leveling in the presence of salt. Reproducible dyeings having the same quality as conventional dyeings were obtained. A limitation noted in the work was the buildup of metal ion content from metal containing dyes. The metal ions were reported to affect shade reproducibility in some dyeings. Since the reconstituted dyebath contains large amounts of salt, this process is probably only applicable to direct dyes which level in the presence of salt.

Experimental Procedures

Ozonation Systems

Kinetic studies and decolorization optimization studies were done in a batch ozone contactor. An ozone-enriched oxygen stream from a Welsbach T-816 ozone generator was bubbled into the test solution in a gas washing bottle through a glass diffuser. The ozone consumption was measured using the standard iodometric method.[11] The effects of variables such as temperature, pH and ozone concentration in the stream on decolorization of dyes we studied in this batch contactor.

Two different designs for contin ous ozone contactors were used. O was a dual column contactor with t columns connected in tandem. Dow flow of dyebath waste and upflow ozone were used. The contactor dime sions and flow directions are shown Fig. 1. The total capacity of each co umn was five liters without packin thus giving a total working volume ten liters. With packing and with th liquid maintained at 3.5 inches abov the packing, the total combined wor ing volume in both columns was 5. liters. Ozone was introduced into co umn 1 countercurrent to the dye wast flow. Flow rate of the dye waste wa controlled by tubing pumps at th points shown in Fig. 1.

The continuous ozone contacto used in the dyebath reuse studies wa a single packed-column design wit downflow of dyebath wastewater an upflow of ozone. In both continuou contactors the ozone utilization wa measured by the iodometric method.

Fabric

The fabric was a 100% cotton knit tha had been previously prepared for dyeing. Batches of fabric weighing te pounds were dyed.

Dyeing Process

Dyeings were performed in a Unimac Tumbler type dye machine. The tub rotated at 20 rpm in all cases. Heating rates were 2, 5 and 10F per minute for the wet-out, dyeing and after washing stages, respectively.

The machine was equipped with a system to collect spent dyebath water and recharge the ozonated (decol-

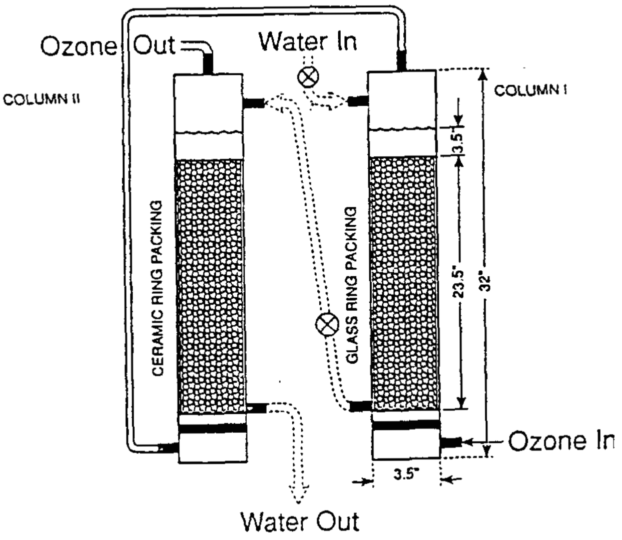


Fig. 1. Dye waste flow.

orized) water to the dye machine on demand. Fig. 2 shows the dyeing and water collection system.

Dyeing Procedures

The dyebath reuse study was done using dye formulations provided by a major textile company for ten commercial dye shades. The ten shades comprised a range of hues across the spectrum and depths ranging from very heavy to pastel colors. The shades included ones considered difficult-to-dye by the company. Table I lists the ten shades and the nineteen dyes used to make them. The shades were dyed in the random order in which they are listed in Table I.

Procedures for Dyeing in Fresh Water

The procedures provided by the participating textile company varied somewhat depending on the depth of shade and type of dye used. The dyeings required three stages—wet-out of the fabric, dye application and washing/rinsing.

Wet-out was done in 15 gallons of water at 90F for 15 minutes. Dyeing conditions adapted from the textile company's procedures were as follows:

For burnt orange shade:
- Add water and fabric.
- Add sodium thiosulfate.
- Heat dyebath containing fabric and water to 105F.
- Add salt and circulate five minutes.
- Add dye and circulate five minutes.
- Add caustic soda and soda ash.
- Dye 45 minutes.
- Drain and pump the spent dyebath to the collection tank.

For dark green and kelly green shades:
- Add water and fabric.

Table I. Dye Shades and Dyes

Shade Name	Dyes Used in Formulation
Burnt Orange	Cibacron Orange C-R Cibacron Scarlet F-3G
Dark Green	Procion Green H-E 4BDA Procion Yellow H-F4R Procion Orange H-ER
Deep Purple	Remazol Blue R-2R Remazol Violet 5R
Black	Remazol Black B Remazol Red RB Remazol Golden Yellow RNL
Light Pink	Remazol Red RB Remazol Golden Yellow RNL
Kelly Green	Remazol Turquoise RP Levafix Brilliant Yellow E-3G Levafix Golden Yellow FG
True Red	Remazol Blue BB New Remazol Orange 3G Remazol Brill Red 3B
Island Yellow	Levafix Golden Yellow EG Levafix Brilliant Yellow E-3G
Royal Blue	Remazol Blue RW Remazol Violet 5R
Sea Mist Green	Remazol Green 6B Remazol Brilliant Yellow 4GL

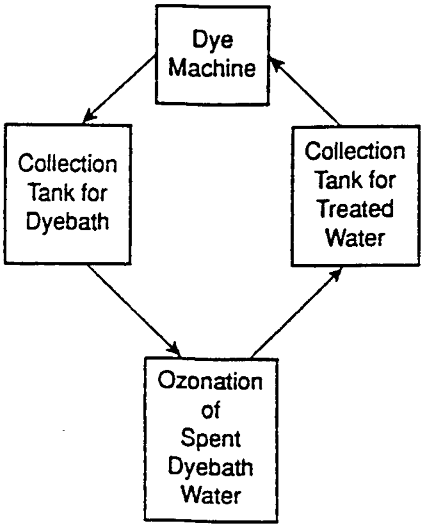


Fig. 2. Dyeing and water collection system.

- Add sodium thiosulfate and heat to 90F.
- Add salt, raise temperature to 100F and circulate five minutes.
- Add dye and circulate ten minutes.
- Add caustic soda and soda ash.
- Raise temperature to 175F and circulate 50 minutes.
- Drain and pump the spent dyebath to the collection tank.

For other shades:
The procedure was the same as that used for the green shades except that the final dyeing temperature was 140F and the final circulation time was 45 minutes. Each afterwash was done with 15 gallons of formulation. The first wash was for five minutes with water at ambient temperature. The fabric was then washed for ten minutes at 120F with acetic acid and a nonionic detergent. The third wash was with water for ten minutes at 175F. Two additional washes were done for five minutes each in ambient temperature water. The fabric was hydroextracted and hung in ambient air to dry.

Procedures for Dyeing in Ozonated Water

The wet out and afterwashing procedures were identical to those used for fresh water dyeings. The dyeing procedures in fresh water and ozonated water differed slightly in the chemical formulations and the way water was added to the dye machine. The pH of the ozonated water was adjusted with caustic soda only since ozonation of the spent dyebath produced carboxyl compounds which had a buffering effect. Before returning the ozonated water to the dye machine, its pH and conductivity were measured to anticipate the amount of additional caustic soda and salt required for the next dyeing. Sodium thiosulfate was added to the reclaimed water in the holding tank. After completion of wet out of the fabric, the dye machine was drained and 6.5 gallons of ozonated water added. Dyeing then proceeded as in the fresh water dyeing procedure. The pH was checked after the initial addition of caustic soda and adjusted, if required, until a pH of approximately 11.0 was achieved. The dyeing was then allowed to proceed to completion.

Dyeing in recycled water required using a standard dye formulation. The formulation used in the study was based on the most common procedures used in commercial practice. The quantities of dyes used were provided by the participating textile company and were exactly the same for dyeings in fresh and ozonated water. The dye formulations and dyeing procedure were as follows:

Formulation for dyeings in fresh water:

Sodium chloride	100 g/L
Caustic soda	(50%)-1 g/L
Soda ash	5 g/L
Sodium thiosulfate	1 g/L
Dye	as in commercial shade

Formulation for dyeings in ozonated water:

Sodium chloride	100 g/L (65% recycled; 35% make up)
Caustic soda (50%)	as required to adjust pH to 11.0
Soda ash	0 g/L
Sodium thiosulfate	1 g/L
Dye	as in commercial shade

Caustic soda, soda ash and sodium thiosulfate were dissolved in water and placed in head tanks. These chemicals were automatically added to the dyebath as designated by the dye cycle program. Salt was added manually as a solid. The total amount of liquid in the dyebath was ten gallons for dyeings in both fresh and ozonated water.

Experimental Dyeing Design

The dyeing and reuse experiments were designed to simulate as closely as possible the reuse of dyebath water in a commercial dyehouse. Each of the ten dye shades was dyed using the procedure described above and the dye formulations provided by the participating textile company.

The spent dyebath water from each of these dyeings was saved and mixed together. A portion of the mixed spent dyebath water was filtered through Whatman no. 1 paper to remove dye particles and lint. The filtered water was ozonated to remove 60-99% of the color and this water was used to dye the first shade (burnt orange). The spent water from this dyeing was filtered and ozonated as before and used to dye the second shade (dark green). This procedure was repeated until all ten shades were dyed in recycled water.

In another series of experiments, samples of the mixed (ten shades) spent dyebath water were decolorized to greater than 98% color removal. This water was used to repeat dyeings that were off shade in the first dyeing in recycled water.

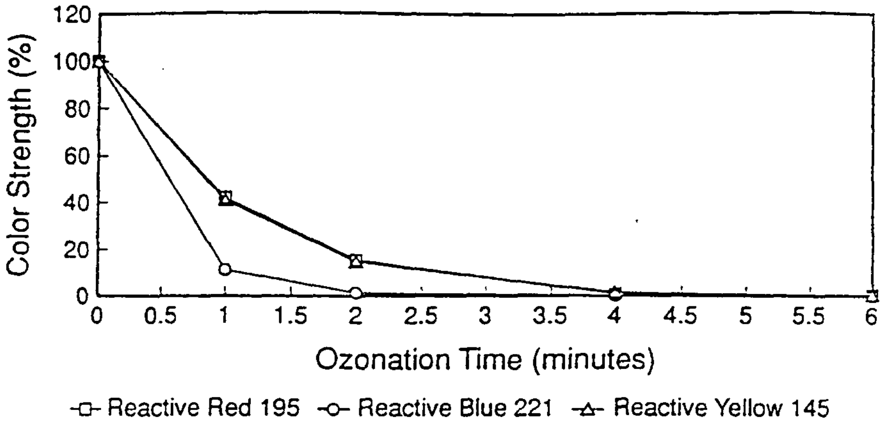
Color Measurements

Color measurements were made on a scanning spectrophotometer. Color strength measurements calculated by the software program provided with the equipment were the ratio, expressed as a percentage, of absorbance of the sample to absorbance of a standard at the wavelength of maximum light absorption of the dye. Color removal values reported in this paper were calculated by subtracting color strength from 100.

Colorfastness Measurements

Washfastness was determined using AATCC Test Method, 61-1989, Colorfastness to Laundering, Home and Commercial: Accelerated. Test conditions were those specified for test number 3A. The results were evaluated spectrophotometrically on a Datacolor International spectrophotometer. The results are expressed as steps on the gray scale for color change and steps on the color transference chart for staining. The analysis program used by the spectrophotometer converted color difference values to these AATCC ratings.

Lightfastness testing was done according to AATCC Test Method, 16-1990, Colorfastness to Light. Both 20-hour and 40-AFU exposures were used. The results were evaluated visually and are expressed as steps on the gray scale for color change.



0.135 g/l dye, 0.5 g/l caustic, ph 11.0
Room Temperature, 2.9 g/hr @ 2.7% ozone

Fig. 3. Decolorization rates of reactive dyes by ozone.

Results and Discussion

Kinetics of Ozonation

Fig. 3 shows rate isotherms for decolorization of three reactive dyes by ozone. The reaction rates were first order with respect to dye. Similar studies were done with vinyl sulfone, monochlorotriazine, chlorofluoropyrimidine and mixed bifunctional reactive dyes. All these types of reactive dyes and other water soluble classes of dyes decolorized rapidly when treated with ozone.

Effect of Temperature

The effect of temperature on the reaction rate of ozone with C.I. Reactive Red 195 was determined in a batch experiment. Color removal rate was slightly greater at 24C than at 50C, but the difference in rates at the two temperatures was small. The difference in color removal by ozone in the temperature range studied would be of little practical significance.

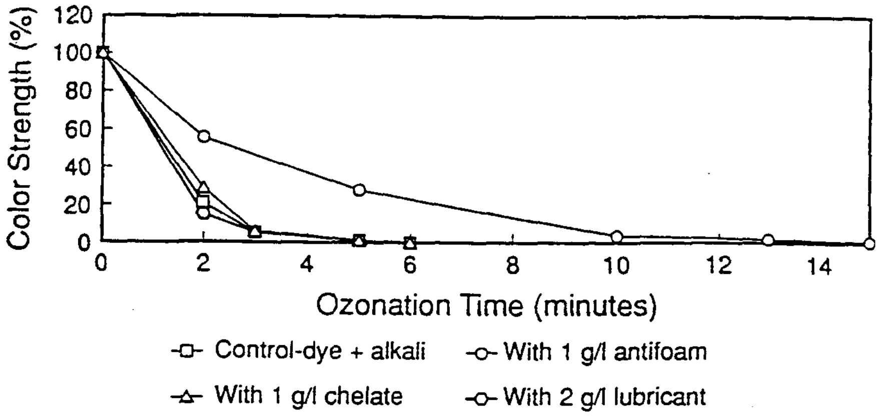
Effect of pH

The effect of pH on the reaction rate of ozone with C.I. Reactive Red 195 was determined in a batch experiment. The initial reaction rate was slightly higher each time the pH was lowered. However, the overall time to achieve complete color removal was the same for each pH studied over the range of 2.5 to 11.25. The observation that pH has only a small effect on the reaction rate of ozone with dyes in aqueous solution seems to support the mechanism of direct reaction of ozone gas with dye molecules at the gas/liquid interface. An aqueous phase reaction involving hydroxyl radicals would seemingly be more pH dependent.

Effect of Jet Dyeing Additives

The effect of dyebath additives on the rate of color removal by ozone was studied in batch experiments. A dye mixture representative of a dark red shade was used. The effect of each additive was observed in a separate experiment. The concentration of additive used was typical of one used in an actual dyebath.

The results in Fig. 4 show that the chelating agent and lubricant had no measurable effect on decolorization of the dye with ozone. However, the silicone type antifoam decreased the initial rate of color removal by ozone by about 50%. The antifoam may contain surfactants which react more readily with ozone than does the dye. Another possible mechanism of the effect of the defoamer in decreasing decolorization rate is that, being surface active, it may interfere with contact of the ozone and dye at the gas/liquid interfaces. Since



1 slpm, 2.9 g/hr at 2.7% ozone
Dyes calculated from liquor ratio of 8:1
and as waste of 10% from plant formula.

Fig. 4. Effect of chelating agent and lubricant on decolorization by ozone.

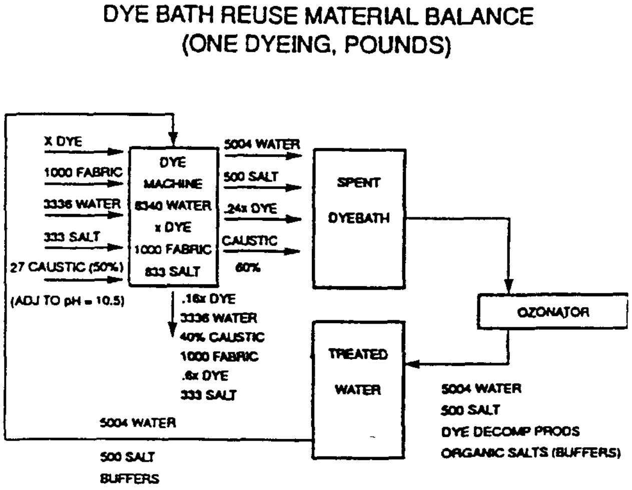


Fig. 5. Dyebath reuse material balance (one dyeing, pounds).

the defoamer interfered with color removal by ozone, the dye formulations used in the dyebath reuse studies contained no defoamer.

Because of concerns that using a defoamer would interfere with successful commercial use of the technology, a trial was performed with a sample of actual spent dyebath water collected near the end of a dye cycle at the participating textile company. The sample of water which contained all ingredients normally used by the company in reactive dyeing was ozonated and used to dye a sample of cloth in a sample jet dye machine. No problems associated with the presence of dyebath additives were found in this trial.

Dyebath Reuse Experiments

Material Balances

The dyebath reuse experiment performed in the study was a 1/100th scale down of the jet dyeing process used commercially. Material balances for the process are shown in Fig. 5 for one dye machine. The calculations giving these balances assumed that all of the color is removed from the water going to ozonation and that complete exchange of liquid is achieved in all washes in the dye machine. As the figure shows, recovery of only the dyebath gives color removal of 60% and salt recovery of 60%.

If both the dyebath and the first rinse water are recovered, color removal increases to 84%. However, only one-half of the water from recovery of the dyebath and first rinse can be reused in dyeing. Therefore, salt recovery is only 42% if both the dyebath and first rinse are recovered and the recovered salt water is reused only in dyeing. Another possible scheme is to use recovered salt water for the final rinse in preparation of the fabric for dyeing. If the ozonated water can be used in the final rinse of the fabric after preparation and before dyeing the next batch, 59% of the salt could be recovered while still achieving 84% color removal from the reactive dyeing wastewater.

Shade Reproducibility

The ten shades were dyed in fresh water and their color compared to standards provided by the participating textile company. The results of these comparisons are shown in Table II. A color difference of < 1.0 DE_{CMC} is usually considered acceptable in commerce. Generally, the standard chemical formulation devised for this work and dye formulations provided by the participating textile company produced fair to good color matches to the commercial standards.

The objective of this work was to determine color reproducibility of dyeing in ozonated water rather than to match the standard shades provided by the company. Therefore, the original dyeings performed at Auburn using fresh water were used as the target shades by which reproducibility was judged.

The ten target shades were then dyed in renovated water by the experimental plan described in the experimental section of this report. The colors of these dyeings were compared to the fresh water dyeings done at Auburn using the textile company's formulations. Results of these comparisons are also shown in Table II. Color reproduction was less than 1.0 DE_{CMC} for four of the ten dye shades. The black and kelly green shades were good visual matches even though the measured color differences were greater than 1.0 DE_{CMC}. The pastel color, light pink, dyed in ozonated water was duller than the dyeing performed in fresh water. Three other shades—island yellow, sea mist green and true red—were judged to be unsatisfactory compared to dyeings in fresh water based on the magnitude of the color difference values and visual evaluation.

These four shades that deviated most from the fresh water dyeings were dyed again in both fresh water and ozonated water which had been decolorized to more than 98% color removal. The colors of these dyeings in fresh and ozonated water were compared. Results of these comparisons are also shown in Table II. The repeat dyeings in ozonated water of light pink, true red and island yellow matched the shade of the dyeings performed in fresh water. The shade of sea mist green was still somewhat different from the corresponding dyeing in fresh water. The results of the dyeing trials suggest that dark shades can be reproduced in ozonated water still containing up to 40% of the spent dye from the previous cycle. Reproduction of

Table II. Color Comparisons

Color Difference (DE) CIE L^*,a^*,b^*
555 CMC (2:1) Sort

Shade Name	Laboratory Dyeings in Fresh Water and Commercial Standards	Laboratory Dyeings in Fresh Water and Ozonated Water	Repeated[1] Laboratory Dyeings in Fresh Water and Ozonated Water
Burnt Orange	0.55	0.52	-
Dark Green	0.68	0.62	-
Deep Purple	2.04	0.98	-
Black	0.29	2.52	-
Light Pink	0.49	2.18	0.66
Kelly Green	2.18	3.06	-
True Red	1.35	2.55	1.03
Island Yellow	2.59	6.59[2]	0.65
Royal Blue	1.17	0.41	-
Sea Mist Green	1.59	3.65	2.27

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[1] Repeat dyeings were done in water ozonated to greater than 98% color removal. [2] The island yellow shade was dull in color compared to the fresh water dyeing due to the fixing of residual color from the dyeing of the true red shade.

pastel colors and very bright shades required a high level of color removal from the spent dyebath water.

Ozonation of the Spent Dyebath Water

The spent dyebath water was ozonated in a 2.8 L capacity column. The flow rate of the spent dyebath was 160 mL/min giving it a dwell time of 17.5 minutes in the column. The ozone concentration was about 1.1% in oxygen and the input rate of ozone was about 9 g/hr. Since the flow rate was held constant, the extent of color removal depended on the concentration of color in the spent dyebath being treated at a particular time. Foaming of the spent dyebath occurred in some cases. No measures were taken to control foam in these studies. Even though defoamers decrease the rate of color removal, the addition of a defoamer during the ozonation stage may be required when the ozonation is done on a larger scale.

Data on pH, color removal by ozonation, ozone consumption and caustic soda requirements for pH adjustment are shown in Table III. The ozone requirement to decolorize the spent dyebath depended on the amount of residual dye in the dyebath and the degree of color removal achieved. Ozone requirement ranged from 558 ppm to 1072 ppm and averaged 821 ppm for the seven cycles in which the water was ozonated once. In three of the cycles, the dye solution was ozonated twice. Including these three cycles, the average ozone consumption was 1068 ppm. The pH decreased during ozonation because of the formation of acidic decomposition products. Since the pH decreased during ozonation, addition of caustic soda was required to adjust the pH in each recycle. The amount of caustic soda required to adjust the pH averaged 2.1 g/L for the ten cycles. Only caustic soda, rather than a caustic soda/soda ash mixture, was used for pH adjustment because the high level of organic acids had a buffering effect on the solution making the soda ash unnecessary.

Table III. Data Concerning the Dyebath Reuse by Cycle

Recycle	Shade Dyed	pH Before Ozone	pH After Ozone	Ozone Consumption (ppm)	Ozone Eff. (%)	Color Removal (%)	Caustic Add-Back (g/L) as 50% NaOH
0	All 10 mixed	9.3	8.7	692	80	90	1.4
1	Orange	11.0	8.3	558	90	83	1.6
2	Dark Green	11.0	8.5	900	95	60	2.7
3	Deep Purple*	11.3	8.8	1590	100	99	2.5
4	Black	11.1	8.7	930	99	72	1.7
5	Light Pink	11.3	10.1	755	85	77	2.2
6	Kelly Green*	11.4	8.6	1540	95	99	2.7
7	True Red*	11.3	7.7	1810	93	98	2.7
8	Island Yellow	11.4	10.6	1072	90	80	1.4
9	Royal Blue	11.4	9.1	843	90	95	2.0
10	Sea Mist Green	11.1	9.0	-	-	-	-

*Ozonated twice. Only 60% color removal was achieved in the first ozonation.

Colorfastness Comparisons

Differences in lightfastness and washfastness between the fabrics dyed in ozonated water and fresh water were not significant.

Economic Evaluation

An economic analysis of spent reactive dyebath renovation was done. Table IV shows the assumptions used in the analysis.

The material balances shown in Fig. 5 for the pilot plant study of dyebath reuse were used as the basis for the economic analysis. The analysis was done for plants running 5, 10 and 20 jet machines. Tables V and VI show the details of the economic analysis.

Savings of salt, water, energy and effluent treatment costs result directly from reuse of warm decolorized dyebath water. Savings in alkali result from the elimination of the need for soda ash (5 g/L). Ozonation of dyes produced buffer-like substances making the addition of soda ash unnecessary. On the other hand, the caustic soda requirement to adjust pH was greater in recycled water (3 g/L) than in fresh water (1 g/L).

A major ozone vendor provided the quotations for equipment for the three systems shown. The quotations were based on data and specifications we provided to the vendor.
The operating cost basis figures used in the calculations were obtained from Ref. 12.

Payback time is shorter for a larger number of dye machines because larger systems have lower equipment costs and lower operating costs per unit of

Table IV. Assumptions Used in Economic Analysis

7200 hours/year plant operation
2.67 batches of fabric dyed per machine per day
1000 pounds of fabric per batch
8.34/1 liquor-to-fabric weight ratio (excluding salt)
60% of dyebath collected after dyeing
750 ppm ozone required to decolorize spent dyebath
2% ozone from air or 4% ozone from liquid oxygen (LOX)
Depreciation—10 years, straight line
Corporate tax rate—50%

Costs:

Salt	$0.05
Caustic Soda (50%)	$0.05
Soda Ash	$0.133
Energy	$4.30/million BTU's
Fresh Water	$1.25/thousand gallons
Effluent Treatment	$1.85/thousand gallons
Electricity	$0.05/kilowatt hour

Table V. Economics of Renovation of Spent Reactive Dyebath Water Using Ozone Generated from Air

	5 Jet Dyeing Machines	10 Jet Dyeing Machines	20 Jet Dyeing Machines
Process Characteristics			
Fabric Production (lb/yr)	4,000,000	8,000,000	16,000,000
Dyebath Ozonated (lb/yr)	20,016,000	40,032,000	80,064,000
Ozone Consumption (lb/yr)	15,012	30,024	60,048
Installed Equipment Cost ($), (tanks, pumps, ozonator, etc.)	180,500	225,000	420,000
Savings ($/yr)			
Salt	100,080	200,160	400,320
Alkali	18,834	37,668	75,336
Water	3,000	6,000	12,000
Energy	4,303	8,607	17,214
Effluent Treatment	4,440	8,880	17,760
Total Savings	130,657	261,315	522,630
Operating Costs ($/yr)			
Electricity	6,906	13,811	27,622
Cooling Water	4,053	8,106	16,213
Labor, Maintenance, Insurance, Taxes	3,453	4,804	8,407
Total Operating Cost	14,412	26,721	52,242
After Tax Payback (years)	2.69	1.75	1.64
Before Tax Payback (years)	1.34	0.88	0.82
Operating Cost Basis ($/pound ozone)			
Electricity	0.46	0.46	0.46
Cooling water	0.27	0.27	0.27
Labor, Maintenance, Insurance, Taxes	0.23	0.16	0.14

Table VI. Economics of Renovation of Spent Reactive Dyebath Water Using Ozone Generated from Liquid Oxygen

	5 Jet Dyeing Machines	10 Jet Dyeing Machines	20 Jet Dyeing Machines
Process Characteristics			
Fabric Production (lb/yr)	4,000,000	8,000,000	16,000,000
Dyebath Ozonated (lb/yr)	20,016,000	40,032,000	80,064,000
Ozone Consumption (lb/yr)	15,012	30,024	60,048
Installed Equipment Cost ($), (tanks, pumps, ozonator, etc.)	107,500	132,000	241,000
Savings ($/yr)			
Salt	100,080	200,160	400,320
Alkali	18,834	37,668	75,336
Water	3,000	6,000	12,000
Energy	4,303	8,607	17,214
Effluent Treatment	4,440	8,880	17,760
Total Savings	130,657	261,315	522,630
Operating Costs ($/yr)			
Oxygen	36,479	53,743	87,670
Electricity	3,753	7,506	15,012
Cooling Water	4,504	4,504	7,806
Labor, Maintenance, Insurance, Taxes	1,051	1,801	3,603
Total Operating Cost	45,787	67,554	114,091
After Tax Payback (years)	2.25	1.28	1.11
Before Tax Payback (years)	1.12	0.64	0.56
Operating Cost Basis ($/pound ozone)			
Oxygen	2.43	1.79	1.46
Electricity	0.25	0.25	0.25
Cooling Water	0.30	0.15	0.13
Labor, Maintenance, Insurance, Taxes	0.07	0.06	0.06

ozone produced. Payback time is shorter for systems based on liquid oxygen (LOX) than for systems based on air even though operating costs are higher for systems using LOX. Operating costs for systems based on LOX are higher because of the high cost of LOX itself. Equipment costs are higher for systems based on air because air preparation equipment must be included in the system.

A dyebath reuse system where only the dyebath is recovered and renovated with ozone gives 60% color removal from the plant effluent. If a higher level of color removal is desired, the first rinse can also be collected and treated for color removal. Color removal of 84% can be achieved if 60% of both the dyebath and the first rinse is collected and treated. However, not all of the treated water can be used in subsequent dyeings because the volume of water renovated is greater than the amount needed in dyeing. This decreases the salt recovery and increases equipment costs for ozone generation and water handling. Therefore, the payback period for the investment is somewhat longer if the first rinse is collected and treated.

Payback and color removal can both be improved if a greater percentage of the spent dyebath liquor can be collected. For example, if capture of the spent dyebath could be improved from 60% to 80%, payback for a system with ten dye machines using LOX would improve from 1.28 years to about 1.02 years assuming that the same water renovation equipment could be used. Color removal would improve to 80%.

Conclusions

Use of ozone to renovate spent dyebaths from reactive dyeing of cotton is technically feasible. Reuse of ozonated water saves chemicals (mainly salt), water, wastewater treatment expense and energy. The savings achieved by reuse of ozonated dyebath water provide after tax payback of the capital investment in approximately 1.28 years for a system using ten jet dye machines and ozone generated from liquid oxygen. Payback for other systems depends on the size of the system, ozone generation method and fraction of dyebath water that can be collected for ozonation. Decolorization of reactive dyes by ozonation was slightly faster at 24C than at 50C. The reaction rate constant for color removal from a solution of C.I. Reactive Red 195 with ozone was 17% higher at 24C than at 50C. The effect of pH on rate of color removal from reactive dye solutions with ozone was small. The difference in color removal rate from a solution of C.I. Reactive Red 195 with ozone was less than 5% over the pH range from 2.5 to 11.25. Presence of a dyebath lubricant and a chelating agent used in reactive dyeing did not affect the rate of color removal with ozone or the amount of ozone consumed. A defoamer used in reactive dyeing decreased the rate of decolorization of the dye by ozone by about 50%. However, the ozone requirement to achieve >90% color removal was not affected by the presence of the defoamer. Quality of dyeings done in spent dyebath water renovated by ozonation was equivalent to that of dyeings done in fresh water.

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