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PROJECT TITLE: Source Reduction of Pollutants from Textile Processing Waste Water

GOAL: The aim of this project and its team is to study techniques that will reduce problems with textile waste water. Techniques examined this year are for removal of color from dye waste by oxidation, electrochemical or membrane filtration, with the ultimate objective of reusing the reclaimed water and its accompanying auxiliaries. Textile manufacturers are experiencing great difficulty in complying with increasingly stringent federal and state regulations concerning waste water. Textile waste water is usually treated to reduce its pollution load after the water leaves the textile plant. However, certain types of pollution (color, heavy metals, and electrolytes for example) are not easily removed by conventional biological waste treatment methods. The purpose of this project is to discover and develop methods to reduce the pollution load at the sources where the pollution is generated within the textile plant. In many cases, source reduction of pollution will be more effective and less costly that conventional waste water treatment.

ABSTRACT: In the ozonation studies, it was shown that the limiting factor in rate is the interface between gas and liquid and that a packed column gave a dramatically more efficient use of ozone. Several reactive dyes were shown to hydrolyze much more slowly than previously thought and that significant unhydrolyzed dye may be present for several hours after dyeing. There is a stoichiometric relationship between the amount of ozone and dye consumed. Electrospray analysis of pure dye and ozonated products showed that the main dye molecule was completely destroyed by ozonation. Toxicity to Duckweed was increased by ozonation and removing the free copper from the ozonated dye decreased its toxicity to about half that of the original dye. An easy and simple chelating method was developed to determine the amounts of free and bound metals in dye mixtures. Oxidation with peroxide and UV was found to be an effective color removal technique. Removal increased proportionally with the UV intensity and there was an optimum concentration of peroxide that increased with the dye concentration. Filtration studies on bleach water and dye waste found that microfiltration removed much smaller molecules (including electrolyte) than was originally thought. Electrochemical color removal of dye from waste water was found to occur by a combination of adsorption and chemical reduction. Singlet oxygen produced by mixtures of hypochlorite and peroxide or by microwave irradiation of oxygen produced significant color loss in unbleached cotton, forming the possible basis for a new zero-effluent bleaching process for textiles.

THE TEAM: Ozonation and peroxide/UV studies were carried out by Perkins, Namboudri and Walsh at Auburn. Product formation during ozonation has been studied by Drews at Clemson and Hill at Auburn. Toxicity methodology was developed by Bennefield, Hill and Ida Reed at Auburn. The microfiltration work was done by Porter at Clemson. Tincher at Georgia Tech was responsible for the singlet oxygen studies and electrochemical removal of dye. The Departments of Chemistry and Civil Engineering at Auburn were involved as well as the textile units at the three Universities.

SPINOFFS AND OUTREACH TO INDUSTRY: A number of projects with industry resulted from the work and expertise gained under this project. Most were funded by sources external to the NTC. Hosiery and sock manufacturers are one of the few segments of the industry that still rely on chlorine for bleaching their final product. It has been believed that it was necessary to use chlorine to achieve the whiteness level essential for consumer acceptance, but researchers at Georgia Tech have developed bleaching protocols based on the more environmentally friendly hydrogen peroxide that equal and even exceed the whiteness formerly achieved with chlorine. Plant trials are planned with Chipman-Union in their Georgia plants at Greensboro and Union Point to demonstrate the new technology which, if successful, will solve a major environmental dilemma facing hosiery and sock manufacturers. Researchers at Clemson are studying returning waste water from the bleaching process automatically for reuse in the initial cleaning of textiles in a continuous fashion. Application of this technology could reduce the total waste water discharged by the textile industry by almost twenty percent. The research is being done in the Clemson plant of WestPoint Stevens in cooperation with plant personnel. Dye waste is also a significant problem in the carpet industry, and Shaw Industries, the largest U.S. manufacturer, is planning a plant trial of a process developed by Georgia Tech researchers to reuse the water from their carpet dyeing machines. Rather than removing the color, it involves adjusting the used dye solution by measuring the residual color and adding just the right amount of fresh dye to make the bath ready for the next carpet. This would ordinarily be too time consuming for practical use, but Tech workers have developed automatic techniques for all the measurements and dye additions, making it possible to quickly ready the waste water for reuse. This not only helps environmentally, but reuses the expensive dye that would be wasted. The project has attracted additional funding from EPA and DOE. EPRI and Southern Company have funded a pilot study on practical reuse of dyebath in reactive dyeing. This study is partially described below. A plant trial based on that study will be carried out at Russell Corporation late this year. About 20 presentations, six publications and two theses have given additional means of transferring this technology to others.

USE OF OZONE TO DECOLORIZE DYEBATH WATER

Continuous Ozonation

Experiments were conducted with packed columns to continuously ozonate reactive dyes in spent dyebath water by using double packed columns each having 2.8 L capacity (excluding packing). Both ceramic and glass raschig ring packed columns were investigated. Color removal and efficiency of ozone utilization improved dramatically with column packing compared to the unpacked column experiments due to improved contact. The effect of dwell time by changing flow rates was studied. The color removal increased as dwell time increased. Changes in pH from 2-11 or small temperature changes from 25-50°C had minimal effect on dye decolorization with ozone. The most efficient use of ozone was achieved by contacting the ozone enriched gas stream with the most concentrated dye solution using packed columns. No significant difference was seen between the two packing types.

Ozonation of Spent Reactive Dyebath water

Spent reactive dyebaths from ten reactive dye shades were ozonated for decolorization after each dyeing prior to the next dyeing for reuse of the dyebath water. These experiments were conducted using a single packed column of 2.8 L capacity at a continuous flow rate of 160 ml/min. which gave a dwell time of 17.5 min. in the column. The ozone flow was 9 g/hr at 1.1 % concentration in oxygen. Color removal from 70 to 99 % were obtained depending on the depth of shade dyed. Out of ten dyebaths three of those required a second ozonation through the columns due to the presence of higher amounts of color. Ozonated dyebath water was reused for subsequent dyeings with great success in reproducing the original dye shades . Cotton fabrics dyed with the decolorized spent dyebath gave comparable color fastness to the fabrics dyed using fresh water. Ozone consumption ranged from 558 ppm to 1072 ppm at an average ozone consumption of 821 ppm. When the dyebath was ozonated twice due to higher amount of color present the average ozone consumption for those baths were 1068 ppm. The pH decreased during ozonation and addition of caustic soda was needed as catalyst for subsequent dyeings. Since salt was already present in the spent dyebath only smaller additions of salt was needed which indicated large savings by the reuse of spent reactive dyebath. (A paper will be presented at the AATCC national meeting in Charlotte , October 11-14,1994 on this subject.)

Ozonation Modelling Studies

The overall objective of this section of the work is to develop a model for the decolorization of water soluble dyes by ozonation which can be used to design more effective decolorization processes. The emphasis has been placed on characterizing the chemical parameters which effect the decolorization of two model fiber reactive dyes by ozone. The dyes chosen included two members of the vinyl sulfone reactive dye class, Reactive Blue 19, an anthraquinone structure and Reactive Black 5 a disazo structure. These dyes were ozonated at two different concentrations (0.10 and 0.25 g/l), at two different pH's (pH=5.9 and pH=10.5) in both their vinyl sulfone and fully hydrolyzed forms. Decolorization was monitored by UV/Vis spectrophotometry. The disappearance of the initial dye species and formation of the degradation products was monitored by HPLC ion pairing chromatography with photo diode array detection. Ozone consumption was continuously monitored using an Orec 3000 ozone monitor. In addition, the pH of the dye solutions was followed during decolorization and cyclic voltametry was used to measure the oxidation potential of the dye solutions before ozonation.

With this experimental set-up, the rate of decolorization was observed to be transport (of ozone across the gas/dye solution boundary) limited. Consequently, it was not possible to determine rate constants for the decolorization of either dye in either form. However, it was possible to measure the ozone consumption and extent of decolorization as a function of time, and in this manner to compare the ozonation of the different forms of each dye as well as the effect of pH on the decolorization chemistry.

The initial HPLC experiments included a brief study of the formation of the vinyl sulfone form of each dye and its subsequent hydrolysis. In these experiments 0.1 g/l dye with 0.27 or 2.7 g/l NaOH solutions were followed by HPLC as a function of time at room temperature, 55 °C and at the boil. For both dyes, the appearance of the vinyl sulfone form and complete disappearance of the initial dye form was observed to occur almost immediately upon treatment with caustic. At room temperature and with 2.7 g/l of caustic it took over 48 hours to fully hydrolyze the vinyl sulfone form of RB 19 and more than 12 hours for the vinyl sulfone forms of RBl 5.

Even at 55 °C, it took more than 4 hours to fully hydrolyze RB 19. From these experiments it was concluded that, in addition to the insight into the mechanism of ozonation and decolorization the presence of the vinyl group in the vinyl sulfone form of these dye would provide, **significant quantities of this dye form would probably be present in the spent dye bath under normal dyeing conditions**.

One of the questions that must be addressed in any mechanistic study of decolorization by the use of ozone concerns the form of the ozone. It has been well established that under neutral to slightly acidic conditions, in the absence of any catalytic agents, ozone is relatively stable in water. Consequently, the decolorization chemistry must result from direct reaction of ozone with the dye molecule. Under alkaline conditions it has been proposed that the presence of the ^-OH ion catalyzes the decomposition of ozone forming a variety of radicals such as $^\cdot OH$, and these are the predominant reactive species. In addition, as the pH becomes more alkaline the oxidation potential of water becomes less positive and the water itself could be more readily oxidized by ozone. In order to rule out this latter possibility, and also to characterize the oxidation potentials of the dyes, cyclic voltametry was performed on the hydrolyzed dye solutions of both dyes at both pH's. At pH = 10.5, only a small rise in the current in the voltamogram was observed at +1.00 V indicating the onset of water oxidation. Under these same conditions, the half wave oxidation potentials of RB 19 and RBl 5 were found to be +0.55 and +0.70 V, respectively. These results show that even at pH = 10.5, the dyes are still the most readily oxidizable species in the solutions.

At this time, the decolorization by ozonation of 0.1 and 0.25 g/l dye solution experiments for both dyes in both forms, at both pH's are in the process of being completed. Based on the results which have been obtained from these experiments to date, some tentative conclusions can be drawn. Perhaps the most significant and, at the same time the least surprising, is that the **overall rate of decolorization by ozone for these dyes is transport limited.** The second is that, for both of these dyes, **it probably requires less than 2 moles of ozone per mole of dye to effectively decolorize them**. Both of these preliminary results further suggest that ozonation can be designed to be a very efficient means of decolorizing water soluble dye solutions.

Electrospray Mass Spectrometry of Phthalocyanine Dyes

An electrospray study of aqueous solutions of phthalocyanine dyes and their decomposition products upon treatment with ozone has been initiated. Typically 1×10^{-4} M solutions of dye in 50/50 acetonitrile/water were subjected to the electrospray conditions. Ozonated solutions were prepared by bubbling an ozone enriched oxygen stream through 1 liter of solution at a flow rate of 2 standard liters per minute (equivalent to 4.32 g of ozone per h) until 90% of the color was removed.

Negative ion mass spectra have been obtained at different skimmer voltages for copper phthalocyanine-tetrasulfonic acid tetrasodium salt, Drimarene K2B®, and Drimarene XG3®. Although specific species cannot (at present) be assigned to all of the peaks, several interesting observations can be made. At a skimmer voltage of -38v, the base peak for all of the unozonated dyes occurs at m/z 207. While identification of this peak with high confidence is not yet possible, this m/z ratio is 64 daltons from that expected for tetrasulfonated dye with no side chain. For all of the untreated dyes only three negative ion peaks are observed at a skimmer voltage of -100v. The most abundant peak at m/z 81 has been tentatively assigned to the HSO_3^- ion.

The ozonated solutions all contain a peak at m/z 97. This has been assigned to the HSO_4^- ion. The m/z 207 peak observed in the untreated dyes is no longer present, **indicating the ozonation completely destroyed the original dye molecule.**

Aquatic Toxicity Tests on Dyes and Color Abated Products

Techniques for measuring toxicity have been extensively developed and the methodology now being used offers high reproducibility and confidence. Toxicity studies have continued using Duckweed tests to bracket toxicities. In general, untreated dyes are relatively non-toxic. All of the metallic dyes tested to date show IC_{50} (inhibiting concentration to reduce the growth rate by 50%) of >500 ppm. However, ozonated solutions of these dyes (at original dye concentrations of 1g/L) produce solutions that have IC_{50} numbers <20 ppm. If the free metal is removed from the ozonated solution, the IC_{50} increases to 200-300 ppm.

DECOLORIZING DYES WITH ULTRAVIOLET LIGHT AND HYDROGEN PEROXIDE

Peroxide and UV

Preliminary UV/Peroxide treatments were made in a batch reactor. The reactor consisted of a two liter graduated cylinder in which was immersed a quartz tube holding the 32 inch low intensity UV lamp. Only 9 watts of radiation was exposed per liter of dye solution. The excess light was blocked by using aluminum foil. The lamp produced radiation at wave length range of 189-254 nanometers of which 90% was at 254 nm. Samples of dye solutions were checked periodically using a spectrophotometer for studying the rate of decolorization.

Eleven dyes were studied representing a broad range of molecular structures (azo, anthraquinone and metalized dyes). The dye classes studied were water soluble dyes such as direct, acid and reactive dyes and water insoluble disperse dyes. Dye concentration was 0.02 g/l in all classes except for the study with reactive dyes where normally the spent dyebath has higher amounts of color present.

The effect of pH was studied using 0.02 g/l Direct Blue 25 and 0.5 g/l hydrogen peroxide (50%). This study revealed that a pH of 6.0 was most effective for dye decolorization with UV/Peroxide. For the water soluble direct and acid dyes at 0.02 g/l dye concentration decolorization was obtained within 15 min and 0.5 to 1.0 g/l of 50% peroxide gave most effective color removal. Since reactive dyebath water contains more color,the effect of color concentration ranging from 0.02 g/l to 0.3 g/l and peroxide concentration ranging from 0 to 5.0 g/l were studied with Reactive Blue 21. This study revealed that maximum rate of color removal was when dye concentration was 0.05 g/l at a peroxide concentration of 3.0 g/l. Optimum peroxide concentration was 3.0 g/l at the highest dye concentration of 0.3 g/l of Reactive Blue 21.

Only limited study was conducted with water insoluble disperse dyes since the rate of decolorization was slow with these dyes. For Disperse Orange 3 an azo dye, 80 % decolorization was obtained in one hour at 0.02 g/l dye concentration and 0.5 g/l peroxide with 9 watts per liter UV radiation, whereas for Disperse Red 60 an anthraquinone dye, only 5% color removal was obtained for the same time period. The rate was three orders of magnitude lower for water insoluble dyes compared to water soluble dyes and only 50% color was removed during three hour treatment for Disperse Red 60.

A detailed kinetic study showed that peroxide increased dye removal by three or four times the rate over UV photolysis alone. The rate constant for ·OH radical reaction (formed by photolysis of hydrogen peroxide) was remarkably invariant over a wide range of dye concentrations. Rates were found to be proportional to UV intensity. A very high intensity bulb has been obtained and it will be determined whether this proportionality holds at these high irradiation fluxes.

Decolorizing Dyes with Peroxide Alone

A study has been initiated on decolorizing dyes with hydrogen peroxide in the absence of UV, at temperatures close to the boiling point of water. The initial study showed that azo and anthraquinone dyes are resistant to decolorization with hot peroxide alone. A copper phthalocyanine based reactive blue 21 was found to decolorize with hot peroxide under neutral pH conditions. The presence of this dye with an azo direct dye and an anthraquinone acid dye revealed that the **copper containing dye catalized decolorization of the other dyes with hot peroxide.** Following this observation a study has been initiated to decolorize the more resistant azo direct dye and anthraquinone acid dye with hot peroxide in the presence of small amounts of copper ions.

FILTRATION

The laboratory filtration unit at Clemson has been used to evaluate the filtering characteristics of JPS/Pepperell bleaching rinse water. The initial results with several samples show that the membrane will foul rapidly, making it difficult to use this type of filter economically. Consequently, the bleaching waste water has been recycled directly to the scouring process with no filtration. This has been done on several occasions manually but not automatically. It will be necessary to control the recycling process so fresh process water can be supplied to the scouring process if problems occur with the bleaching rinse water. Control of the rinse water recycling will be accomplished using a conductance probe inserted in the bleaching rinse water discharge to measure the level of impurities present in the bleaching rinse water. The conductance reading will be attached to the existing control process for the preparation range. When contamination reaches an undesirable level, the process water flow going to the bleaching wash boxes can be increased to provide better washing. This will allow the water supply to bleaching wash boxes to be optimized and based on fabric needs. The control process will also respond to the needs of the scouring wash boxes and increase the water flow if insufficient water flow is being supplied to the scouring wash boxes. Data is being collected to identify process water consumption before and after the recycling process is installed to document water savings. Several waste water samples have been taken and no problems are anticipated for the recycling process. The automated system should be in operation before the end of 1994.

Data which has been collected on the microfilter (0.2 u porosity, 2000 A) supplied by DuPont revealed that the microfilter was rejecting from 10 to 50% salt or conductivity. This was surprising because the filter was only designed to remove particulate or fine suspended solids. The filter was operated at 100 psia and gave filtration rates of 50 to 300 gallons/ft^2/day at temperatures of 25 to 60 °C. Because of the possibility of using microfiltration in many textile dyeing and finishing operations, it was decided to investigate the filtration characteristics of the stainless steel microfilter more closely to gain a better understanding of the process. Both tap water and deionized water were used for the initial investigation. Representative results from these experiments clearly showed **electrolyte was being rejected by these membranes.** To investigate the mechanism of membrane rejection of the electrolyte in more detail, soluble acid and direct dyes were selected for study at three different temperatures. This was done to find out what effect molecular size has on the rejection process. It has been commonly assumed that salts and nonpolymeric compounds could not be separated by microfiltration. However, the development of microfilters with very small pores, <= 5000 A° (0.5 u), may change our idea of what is possible with this type of filter. The results from these experiments were very encouraging and more work is being done with ceramic membranes to understand and confirm the data obtained with a TiO2 membrane on porous stainless steel.

SINGLET OXYGEN BLEACHING OF COTTON

Although dyeing waste water receives the greatest attention in environmental research, preparation processes are more highly polluting, require extensive treatment systems and will be a greater barrier to achieving closed loop textile processing. Bleaching is the most complex and least understood of the preparation processes. There is not even general agreement on the "active" chemical species responsible for cotton bleaching by hydrogen peroxide despite the fact that hydrogen peroxide is used in over 80% of fabric preparation processes. This lack of understanding of the process has led to primarily "trial and error" experiments in designing bleaching systems.

One of the species that has been suggested as the active agent in hydrogen peroxide bleaching systems is oxygen molecules in the singlet state. This oxygen species is known to react rapidly with carbon-carbon double bonds and to be formed under some bleaching conditions. The current research is directed toward defining the role, if any, of singlet oxygen in cotton bleaching and to determine if textile bleaching systems based on singlet oxygen can be developed.

Initial experiments were conducted on chemical systems for generation of singlet oxygen. The reaction of sodium hypochlorite with hydrogen peroxide was investigated and the singlet oxygen produced detected by the emission of singlet oxygen (chemiluminescence) at 634 nm. Initial experiments were conducted to determine the dependance of singlet oxygen production in the NaOCl and H_2O_2 reaction on pH and temperature.

Conditions were then selected to compare whiteness of cotton socks bleached under conditions in which singlet oxygen was produced and in the absence of singlet oxygen. In the presence of singlet oxygen there was **an increase of 3 units in whiteness over bleaching conditions in which no singlet oxygen was produced.**

In recent experiments, cotton socks were exposed to microwave generated singlet oxygen in a gas phase bleaching experiment. Again, **a 3 unit increase in average whiteness was observed.**

These experiments suggest that singlet oxygen is capable of bleaching cotton and could form the **basis of a new zero-effluent gas phase bleaching process for textile products.**

ELECTROCHEMICAL REMOVAL OF COLOR FROM REACTIVE DYEING WASTE WATER

A number of recent studies have suggested electrochemical treatment as a viable mechanism for removal of color from textile dyeing waste water. In the electrochemical treatment process, the dyeing waste water is passed through an electrochemical cell containing cold rolled steel electrodes. Ferrous ions are produced at the anode and hydroxyl ions at the cathode to give a precipitate of ferrous hydroxide with a very active surface. In addition to adsorption, it has been demonstrated that **some dyes are chemically reduced in the electrochemical process.** It has not been determined whether this reduction process is a direct electrode reaction at the cathode or a reduction by the ferrous ions produced at the anode. The current work is directed toward providing a better understanding of the fundamental removal mechanisms which could led to improved electrochemical color removal processes.

Four reactive dyes representing a range of typical structures were selected for study. Details of the structures of the dyes are shown in Table 1. The dyes were prepared in the reacted form that would be present in waste water by heating to 30 C for 1 hour in the presence of sodium carbonate. Salt and a chelating agent were added to the dye solutions to simulate the conditions that would be present in typical reactive dyeing waste water.

TABLE 1
Reactive Dyes Selected for Study

DYE	REACTIVE GROUP	BASIC STRUCTURE
Reactive Blue 19	**Vinyl sulphonyl**	**Anthraquinone**
Reactive Red 2	**Dichlorotriazinyl**	**Monoazo**
Reactive Yellow 15	**Vinyl sulphonyl**	**Monoazo**
Reactive Blue 4	**Dichlorotriazinyl**	**Anthraquinone**

After exposure in the electrochemical cell, 200 ml samples of each dye solution and control were collected and processed for analysis.

The results of the electrochemical treatment in per cent of original color removed in the process as a function of the mg/l of ferrous iron added are given in Table 2.

TABLE 2. Electrochemical Removal of Reactive Dyes

FE(mg/l)	RB19	RR2	RY15	RB4
10	82	55	75	54
10	86	43	79	50
50	85	48	74	51
100	82	61	76	54
100	86	55	79	52
300	86	101	89	55
500	98	96	95	61

It is apparent that the removal of the two vinyl sulphonyl dyes (RB 19 and RY 15) occurs more readily than the removal of the dichlorotriazinyl dyes. The simulated spent dyebaths are somewhat different for these two types of reactive dyes (salt concentration is higher for the vinyl sulphonyl dyes and the dichlorotriazinyl dyes have a small quantity of EDTA chelating agent) reflecting the different conditions in the dyebath. These differences may be responsible for the increased removal of the vinyl sulphonyl dyes. The increased removal could also be related to the differences in the structures of the reacted groups on the dyes. The vinyl sulphonyl dyes have a $\text{-SO}_2\text{-CH}_2\text{-CH}_2\text{-OH}$ group and the dichlorotriazinyl dyes have an -OH group on a heterocyclic ring. These structure differences may influence the color removal.

There does not appear to be a consistent pattern of color removal in relation to the chromophore structure. In the case of the vinyl sulphonyl dyes, the anthraquinone and monoazo dyes appear to be removed to about the same extent but in the dichlorotriazinyl dyes the monoazo is more readily removed. More information is clearly needed on the relationship between dye structure and color removal.

The data are also interesting in that low levels of iron remove substantial quantities of color but **there is no clear-cut relationship between amount of ferrous ion added and the color removal**. This may be a further reflection of the complexity of the color removal process. It has been demonstrated that, in addition to the removal of color by coagulation and sedimentation, **some color is removed by reduction processes in the electrochemical cell that chemically cleave dye molecules.** The reduction may also be achieved by reaction of dye with the ferrous iron generated electrochemically). It was also observed that the actual amount of ferric hydroxide present in the samples varied significantly with the dye waste water being treated. Thus, a variety of competing and/or sequential color removal mechanisms may occurring in the electrochemical cell. It is clear that future experiments must give more careful attention to dye structure, the exact composition of typical spent dyebaths and the specific conditions of operation of the electrochemical cell is evaluating dye removal.

SELECTED PUBLICATIONS AND PRESENTATIONS

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2. W.S. Perkins, C.G. Namboodri, and W.K. Walsh, **Decolorizing Dyes with Ozone and Chlorine,** In Chemical Oxidation Technology for the Nineties, Volume 3, Technomic Publishing Company, Inc., Lancaster, p. 202-215.

3. W.E. Hill, W.S. Perkins, and G.S. Sandlin, **Removal and Speciation of Transition Metal Ions in Textile Dyeings Waste Waters,** Textile Chemist and Colorist, Vol. 25, No. 11, November, 1993, 26-27.

4. Chen Keqiang, W.S. Perkins, and I.E. Reed, **Dyeing Cotton with Reactive Dyes Using Ozonated, Spent Dyebath Water,** Textile Chemist and Colorist, Vol. 26, No. 4, April, 1994, 24-28.

5. C.G. Namboodri, W.S. Perkins and W.K. Walsh, **Decolorizing Dyes with Chlorine and Ozone: Part I,** American Dyestuff Reporter, Vol. 83, No. 3, March, 1994, p. 17, 18, 20, 22.

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7. C.G. Namboodri, W.S. Perkins and W.K. Walsh, **A Comparative Study of Ozone and Ultraviolet Light/Hydrogen Peroxide for Decolorizing Textile Dyeing Waste Water,** Proceedings of the Sixteenth National Industrial Energy Technology Conference, Houston, Texas, April 13-14, 1994.

8. A. Nieder, **The Ozonation of the Vinyl Sulfone and Hydrolyzed Forms of Reactive Blue 19 and Reactive Black 5,** MS Thesis directed by M. Drews, Clemson University, October, 1994 (to be submitted).

9. N. Huang, **Kinetics of Photolysis of Reactive Dyes in the Presence of Hydrogen Peroxide**, MS Thesis directed by W. Perkins, Auburn University, June 8, 1994

10. W. Tincher, **Electrochemical Removal of Color from Reactive Dyeing Waste Water,** ACS Symposium on Emerging Technologies in Hazardous Waste Management, Atlanta September, 1994.

11. C. Namboudri, **The Use of Peroxide and Ultraviolet Light to Remove Color from Dyeing Waste Water,** ACS Symposium on Emerging Technologies in Hazardous Waste Management, Atlanta September, 1994.

12. J. Porter, **Filtration Studies of Selected Textile Waste Streams Using Asymmetric Metal Oxide Membranes on Porous Stainless Steel Tubes,** Engineering of Membrane Processes, Conference proceedings, Tuscany, Italy, April 26-27, 1994

13. J. Porter and R. Porter, **Filtration Studies of Selected Anionic Dyes Using Asymmetric Titanium. Dioxide Membranes on Porous Stainless Steel Tubes,** Membranes and Filtration Systems Conference, Monterey, California, July 28-29, 1994 (submitted to the Journal of Membrane Science for publication).