

Spectrophotometric Analysis of Electrochemically Treated, Simulated, Disperse Dyebath Effluent

LARGE quantities of water, dyes and chemicals are used in textile wet processing, and safe, economical disposal of this aqueous waste poses considerable difficulty. Wastewater from dyeing is a problem not only because of its potential toxicity but also because it may contain residual color which acts as an aesthetic pollutant (1). When one considers that dyebath effluents contain a complex mixture of dyes, dispersing agents, leveling agents, wetting agents and trace metals (2-5), it becomes obvious that every effort must be made to minimize the amount of waste released into the environment.

In the United States and Canada, various levels of government have imposed increasingly stringent regulations governing the amount and type of waste material that can be sent into the environment (6). Furthermore, in some municipalities, the cost of water and the treatment of effluent

ABSTRACT

A series of experiments was conducted to characterize disperse dye effluent after electrochemical treatment with aluminum electrodes. Two anthraquinone, two azo and two quinoline dyes were used in combination with the commonly used dispersing agents (naphthalene sulphonate and ligninsulphonate) usually blended with these dyes. The results showed that the treatment removed at least 98% of the original color but not all the dye auxiliaries/dyebath assistants. Of the dispersing agents, the naphthalene sulphonate was more difficult to remove than the ligninsulphonate. Data suggest that the mechanism of electrochemical treatment with aluminum electrodes is one of physical adsorption rather than dye destruction.

KEY TERMS

Disperse Dyes
Dispersing Agents
Dyebath Reuse
Electrochemical Treatment
Ligninsulphonate
Naphthalene Sulphonate
Wastewater

The Winning Entry

The Hudson-Mohawk Section was the only entry in this year's Intersectional Technical Paper Competition at Atlanta last month. This is the first time in the event's history that only one entry was received.

have soared to the point that mills must reduce their waste usage and optimize their own treatment processes if they are to survive. Reuse of decolorized dyebath effluent has been shown to be economically viable (7-14), particularly if used in combination with computerized colormatching systems.

At present, there is no method to economically and reliably decolorize and/or detoxify textile mill effluent. Biological degradation, chemical coagulation and reverse osmosis have been shown either to be inadequately effective or uneconomical (1,15-17). Carbon adsorption and ozonation of dyebath effluent (the major pollutant) results in poor color removal, particularly of disperse dyes (16).

Electrochemical treatment of colored effluent has received some attention in recent years (14,17-21). Two authors independently reported two different methods for electrochemical separation of effluent but neither gave details of the equipment nor documented the actual success of their treatments (22, 23). The scant literature focuses on applications of electrochemical techniques to decolorize those dyebaths containing acid or disperse dyes because of the prevalence of these two dye classes. Only one study (19), however, considered the mechanism by which electrochemical treatment might work, and attempted to identify the resultant breakdown products that could be released into the environment or be contained within recycled decolorized effluent. Using HPLC techniques, these researchers concluded that the electrochemical separation of an aqueous solution of pure dye resulted from absorption and/or degradation of the dye itself, following interaction with iron electrodes. In that same study, degradation of one of the two azo dyes that were studied resulted in the formation of potentially toxic aniline. The degradation

product(s) of the other azo dye was (were) not specifically characterized. Apparently, no breakdown products were found in the successfully treated effluent that originally contained an anthraquinone dye. No attempt was made to examine the efficacy of electrochemical treatment of components, other than the colorant, which normally are found in any commercial dye.

The task of fully characterizing the colorless effluent is a complex but important one. The dyes themselves are complex (usually proprietary) chemical mixtures, and the addition of various additives to the dyebaths further adds to the list of chemicals that may remain as contaminants of the innocuous appearing colorless supernatants following electrochemical treatment. Some of these chemicals may be toxic or carcinogenic, or in the very least, may interfere with the utility of this supernatant when reintroduced into the dyeing or finishing processes.

In this study, we investigated the effect of electrochemical treatment on simulated commercial dyebath effluent, and subsequently analyzed the colorless effluent for traces of dye or dyebath chemicals other than the colorant itself.

Materials and Methods

Dyes

The dye concentration used in the majority of studies was 0.25% weight/volume. Other chemicals were added to give concentrations equivalent to those estimated to be present in medium shade, exhausted disperse dyebaths.

Six disperse dyes were selected for use because they had well characterized chemical structures and formulations and their chemical structures were representative of disperse dyes in general use today. Two of the dyes were anthraquinone, two were azo and two were quinoline (Table I). The dispersing agents used with these dyes differed (Table I), and one of the sections in this study isolated the effects of these agents from those of other portions of the dyebath.

Assistants

The following chemicals, considered typical of commercial disperse dyebath assistants, were used in most of the experi-

Analysis of Dyebath Effluent

ments. To simulate a commercial disperse dyebath, a 10 mL aliquot of the assistant solution (chemical system) was added to each 500 mL of dyebath:

2.0% owf C.N.C. Carrier MB (C.N.C. International), *o*-chlorotoluene containing diphenyl

1.0% owf Tetralev (Reilly Whiteman Inc), nitrogenous complex leveling agent

0.6% owf C.N.C. Defoamer 544-C (C.N.C. International), silicone glycol polydimethyl siloxane

0.5% owf Basojet PEL-200 (BASF Corp.), nonionic/anionic surfactant mixture

0.25% owf Nirex LF-50, (Leatex Chemical Co.), surfactant-ester blend

0.1% owf acetic acid

Electrochemical Cell and Treatment Procedure

The electrochemical cell that was used to treat all dyebath effluents consisted of four aluminum plates joined by polyvinyl chloride and Teflon nuts, bolts and washers so

that there existed a space of approximately 0.5 cm between adjacent plates. Aluminum electrodes were chosen to minimize the risk of chemical reduction of dye or additives, which creates an unnecessary risk of harmful breakdown products. A DC power supply was connected to the outermost plates, causing the plates to act as electrodes upon application of current.

Treatment consisted of placing the electrodes in a 500 mL sample containing the dye(s) and chemical(s) of interest. The initial pH of the bath was adjusted to 4.0 ± 0.1 , a close approximation of that of exhausted disperse dyebaths. The liquor was stirred with a magnetic stirrer to move it through the gaps between the aluminum plates. When an electrical current (0.4 amperes) was applied, aluminum ions were released from the positively charged sides of the electrodes; i.e., the aluminum plates. The following calculation, based on Faraday's Law, was used to determine the amount of aluminum released during treatments of different durations:

$$\text{ppm Al} = (\text{time (min.)} \times \text{amps} \times 1.4778 \times \text{no. of gaps between electrodes}) / \text{volume (gal.)}$$

Aluminum generation ranged from 81.8 to 327.4 ppm for treatments varying from 6 to 24 minutes (Table II).

Table II. Amount of Aluminum Generated During Electrochemical Treatment of Various Durations¹

Treatment Time	Aluminum Generation
6 min	81.8 ppm
8	109.1
10	136.4
12	163.7
14	191.0
18	245.5
24	327.4

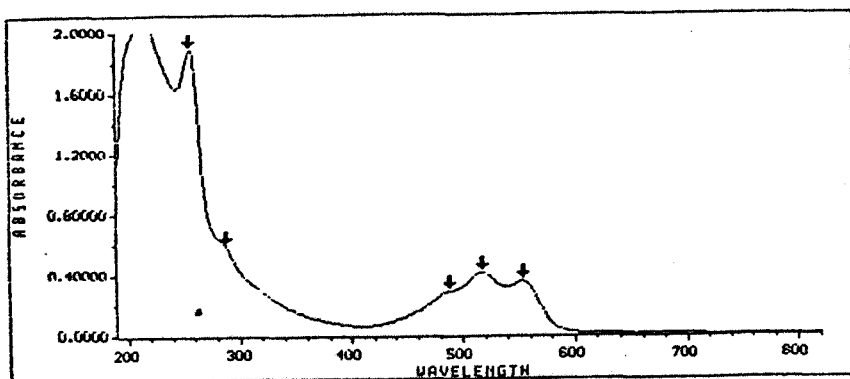
¹Aluminum generation was calculated only for treatment times used in this research.

The pH of the liquor was allowed to fluctuate during the application of the current, which was followed by a 15 minute degassing period designed to release the small amount of hydrogen gas generated during treatment. The pH was then adjusted to 6.2, the minimum solubility of aluminum, and a small amount (0.3 mL) of nonionic polymer (Magnifloc

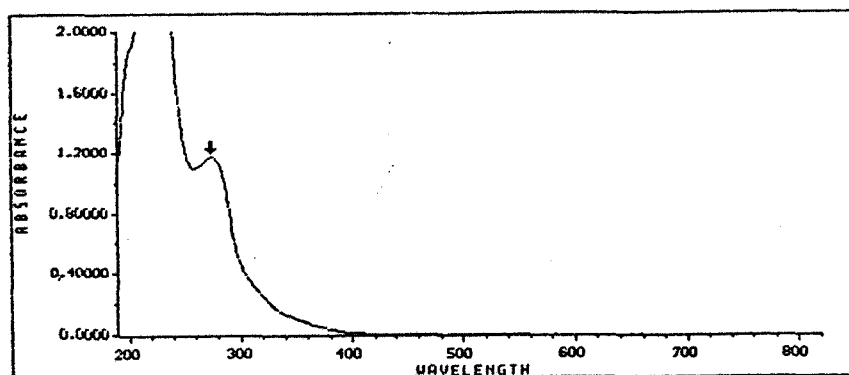
Table I. Description of Commercial Dyes¹

C.I. Name	C.I. Number	Dispersing Agent ²	Chemical Structure
Anthraquinone: C.I. Disperse Blue 60	506415	A (48%) + B (28%)	
C.I. Disperse Red 263	500931	C (60%) + B (12%)	
Azo: C.I. Disperse Blue 148	500821	B (56%) + A* (3%)	
C.I. Disperse Orange 73	506178	B (59%) + A* (1%)	
Quinoline: C.I. Disperse Yellow 54	500681	B (35%) + A (10%)	
C.I. Disperse Yellow 64	500631	C (54%) + A (9%)	

¹All dyes were manufactured by BASF. ²A = Naphthalene sulphonate; B, C = Ligninsulphonate derivatives. A* = Similar to A.

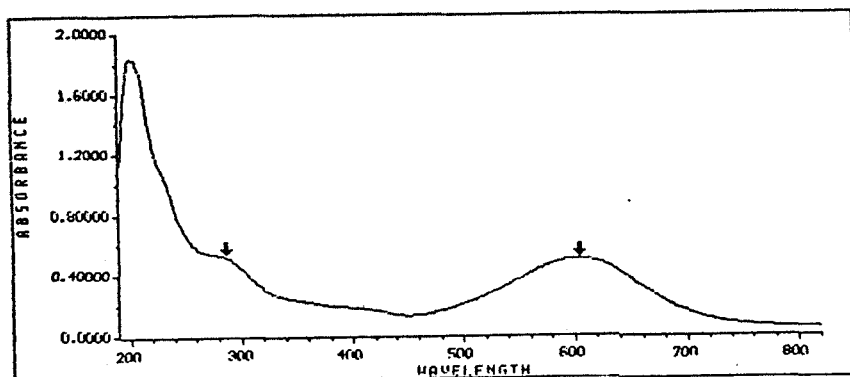


(a)

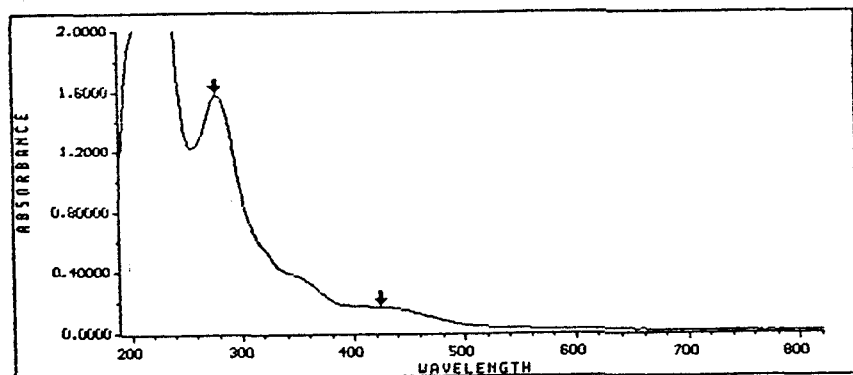


(b)

Fig. 1. Spectrophotometric curves of C.I. Disperse Red 263 (a) before and (b) after treatment for 12 minutes (dilution 10/250, 50/100, respectively).



(a)



(b)

Fig. 2. Spectrophotometric curves of C.I. Disperse Blue 148 (a) before and (b) after electrochemical treatment for 12 minutes (dilution 1/100, 50/100, respectively).

of 12 minutes (163.7 ppm aluminum) was selected as the best treatment time overall.

Yellow 64 showed peaks in the visible region at 420 and 436 nm (Fig. 3), the latter being the standard for strength adjustment. After treatment for six minutes, the spectral curve remained above the baseline although no peak was registered. Turbidity was evident in the sample that had been treated for 8 minutes. As was true with Blue 148, increased treatment times caused a progressively decreasing amount of dispersing agent, this time up to 10 minutes. A 10-minute treatment time was determined to be optimal, corresponding with an aluminum generation level of 136.4 ppm.

● Experiment 2: Effect of Electrochemical Treatment on Dispersing Agents with and without Colorant. It is likely that dye additives, particularly the water soluble dispersing agents, are not exhausted during dyeing at the same rate as the colorant within the dye. Therefore, the efficacy of the electrochemical treatment in removing these agents per se was determined. The dispersing agents were also combined with one anthraquinone, one azo and one quinoline colorant to determine whether there is an interaction between dispersing agent and colorant that influences the efficacy of treatment.

A 2.5% solution of each dispersing agent [identified only as naphthalene sulphonate ("agent A") and ligninsulphonate ("agent B" and "agent C")] in distilled water was prepared and electrochemically treated for 12 minutes.

Each of the crude colorants of Red 263 and Blue 148 was dry blended with the main ligninsulphonate dispersing agents normally used in each of these commercial dye formulations (Table I). Similarly, a second blend of each was prepared by substituting the ligninsulphonate with an equal amount of naphthalene sulphonate dispersing agent. Yellow 64 crude colorant was dry blended with the two dispersing agents used in the commercial formulation as well as with an equivalent amount of pure naphthalene sulphonate. The ratio of colorant to dispersing agent was that used in the commercial dye although the exact proportion of each cannot be disclosed in this paper for proprietary reasons.

The six blends of crude dye and dispersing agent were solubilized by adding 30-40 mL of dimethylformamide (DMF) to dissolve the crude dye component, subjecting the dispersions to ultrasound for 5 minutes and then increasing the volume to one liter with distilled water. The dispersions were treated for the optimal treatment times (as established in Experiment 1 above). If necessary, the time was lengthened in order to achieve total clarification. Spectral analysis was done to establish the percent of original dispersing agents remaining in the treated effluents.

After treatment, the naphthalene sulphate (agent A) had 90% of its original components. Similarly, 88% (agent B) and 82% (agent C) of the original components of the ligninsulphonate samples remained (Figs. 4-6).

The 12-minute optimal treatment time was of insufficient length to decolorize the bath containing crude Red 263 and ligninsulphonate. The processing time was increased to 18 minutes at which time no color remained. In the UV region of the spectrum, a peak at 232 nm was reduced to approximately 8% of its original height following treatment. This peak was present in all spectra in this experiment and it was attributed to the DMF solvent. It will not be included in further discussions of these spectra. Approximately 10% of the original amount of ligninsulphonate, absorbing at 278 nm, remained after the 18-minute treatment (Table V).

The 18-minute treatment, which successfully removed all the color in the sample containing Red 263 and ligninsulphonate, did not decolorize the bath containing colorant blended with naphthalene sulphate. Furthermore, when the bath containing naphthalene sulphate and colorant was filtered following treatment, the particles of flocculent were smaller than those formed following filtration of the bath containing the colorant and ligninsulphonate. (This difference in particle size was observed with the red colorant but not with the blue or yellow.) The greater total surface area of the smaller particles in the bath with naphthalene sulphate may have interfered with the efficiency with which the aluminum electrodes were able to adsorb particles. A longer treatment time (24 minutes) decolorized the dispersion to meet our standard of $\leq 2\%$ residual color. The naphthalene sulphate dispersing agent was more difficult to remove than its ligninsulphonate counterpart, with about 14% remaining after the 24-minute treatment period (Table V).

As with Red 263, the time required to decolorize the sample containing Blue 148 and ligninsulphonate exceeded the optimal treatment time determined for the commercial formulation of this dye. Total removal of the peak indicative of blue (604 nm) was achieved only after 18 minutes. The peak at 428 nm (yellow), which had occurred in all previous treatments of this dye, was once again present. In the UV region, a peak at 280 nm indicated that approximately 9% of the ligninsulphonate present before treatment remained afterwards (Table V).

The 18-minute treatment established for the blend of the crude Blue 148 colorant and ligninsulphonate successfully decolorized the sample containing the same crude colorant and naphthalene sulphate. Once again, the treated bath was yellow (peak at 440 nm). The naphthalene sulphate peak indicated that 7%

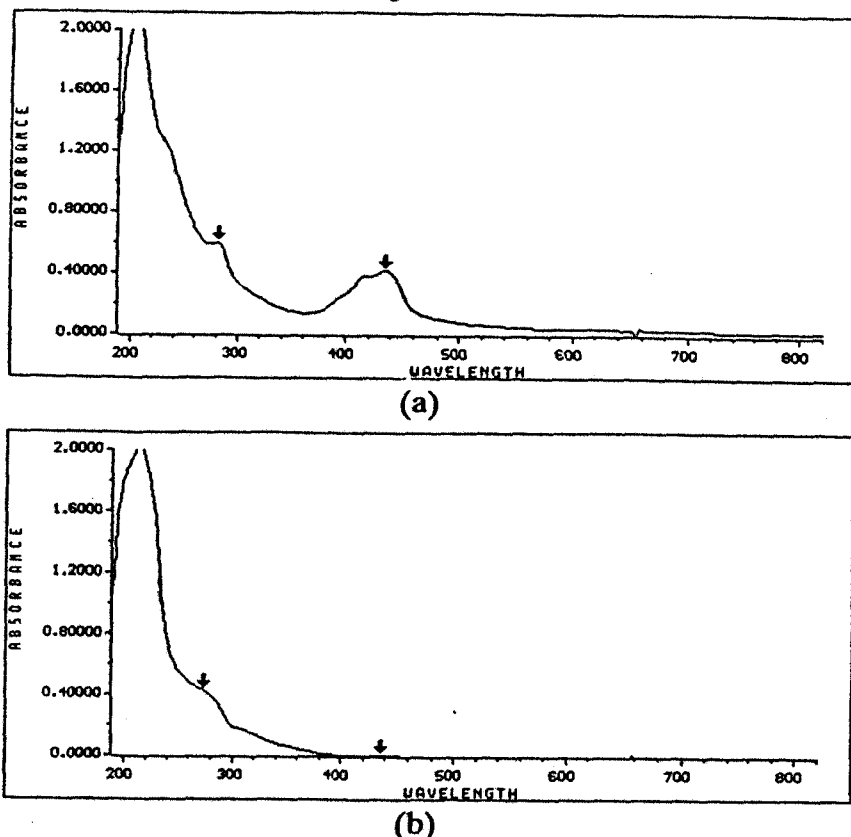


Fig. 3. Spectrophotometric curves of C.I. Disperse Yellow 64 (a) before and (b) after electrochemical treatment for 10 minutes (dilution 2/100, 50/100, respectively).

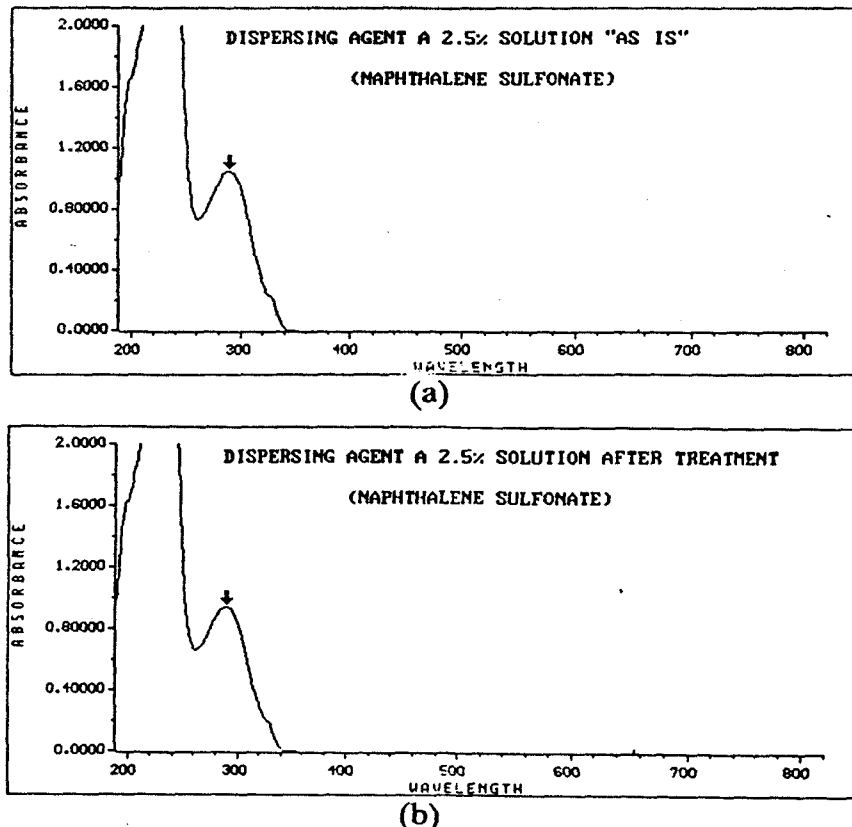
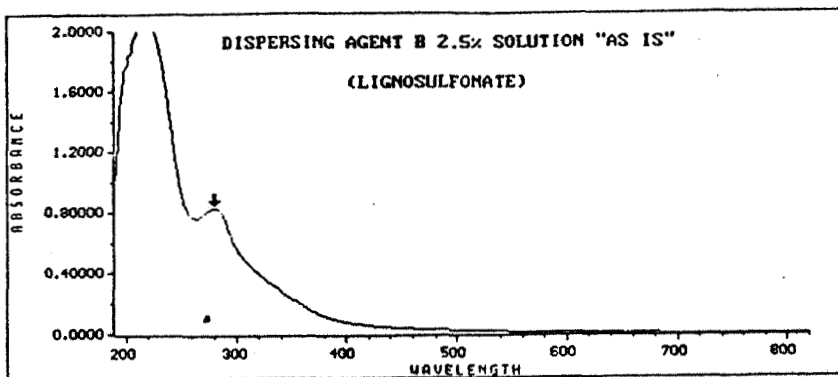
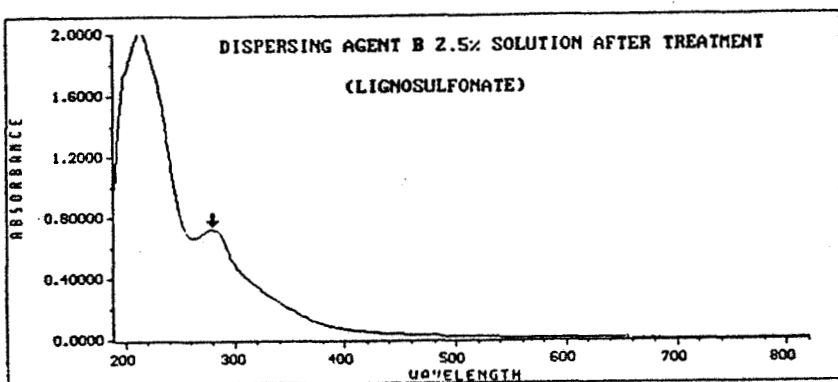


Fig. 4. Spectrophotometric curves of naphthalene sulphate (agent A) (a) before and (b) after electrochemical treatment for 12 minutes (dilutions of both: 1/500).

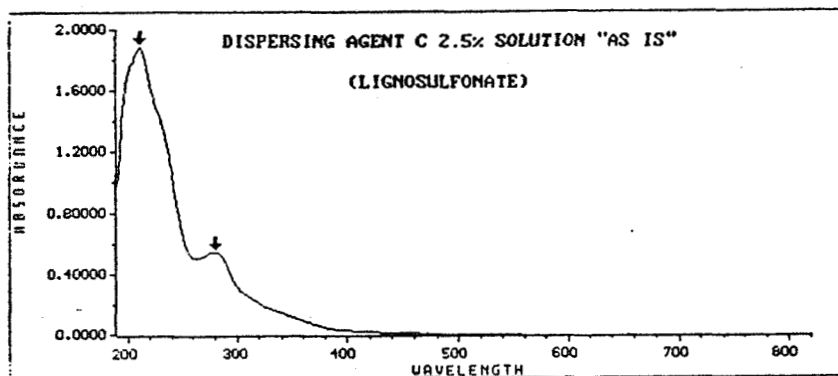


(a)

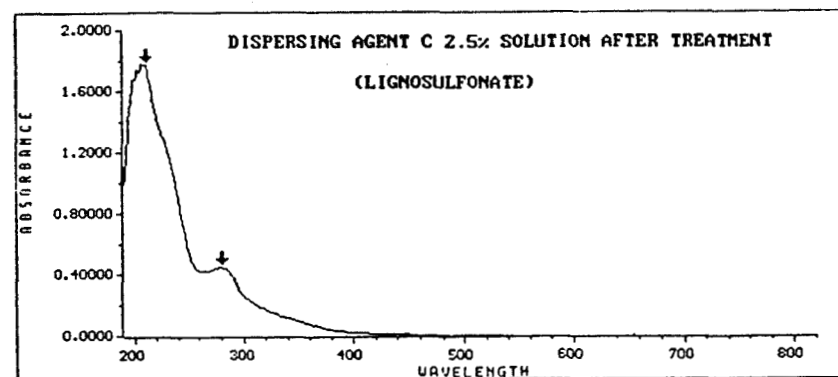


(b)

Fig. 5. Spectrophotometric curves of ligninsulphonate (agent B) (a) before and (b) after electrochemical treatment for 12 minutes (dilutions of both: 1/500).



(a)



(b)

Fig. 6. Spectrophotometric curves of ligninsulphonate (agent C) (a) before and (b) after electrochemical treatment for 12 minutes (dilutions of both: 1/500).

remained following treatment (Table V).

The crude Yellow 64 colorant blended with ligninsulphonate and naphthalene sulphonate was decolorized with the optimal 10-minute treatment time previously established for this dye. There was 17% residual dispersing agent composed of ligninsulphonate and naphthalene sulphonate (Table V), with the key wavelengths too close to permit their differentiation. A longer treatment time, comparable to that used with Red 263 and Blue 148, may have decreased the residual amount of dispersing agent.

The 10-minute treatment totally decolorized the mixture of Yellow 64 and naphthalene sulphonate. The peaks at 284 and 276 nm before and after treatment indicated approximately 18% residual naphthalene sulphonate (Table V), which may have been less had the treatment time been comparable to that of the other mixtures in this experiment.

With two of the three colorants (Blue 148 and Yellow 64), the nature of the dispersing agent had little effect on the removal of dispersing agent by electrochemical treatment. The reason for the formation of the small particles of Red 263 after treatment, which is believed to have interfered with the rate and completeness of the reaction, is unknown.

The rate of removal of dispersing agent alone compared to that of the dispersing agent plus colorant differs greatly (Table V), suggesting that there exists an interaction between the two. This is consistent with the theory that particles of dispersing agent are electrostatically bonded to the colorant; it is reasonable that these complexes of colorant and dispersing agent would be removed as such. It can be inferred from our results, therefore, that the chemical nature of the dispersing agent, the amount of dispersing agent present, as well as other components such as colorant, have a marked effect on the rate of removal of dispersing agents.

● Experiment 3: Comparison of Electrochemically Treated Dyebaths with and without Dyebath Assistants. Since dyebath assistants such as carrier facilitate the dyeing process, it is reasonable to assume that they also have an effect on the efficacy of electrochemical treatment. Spectra of simulated effluents with and without dyebath assistants (chemical systems) were compared.

Twelve-minute treatment of the baths containing Red 263 with and without the chemical system resulted in total color removal in both cases. In the absence of the chemical system, some turbidity was apparent in the treated bath.

In the UV region, the treated bath containing Red 263 without chemicals contained only about 6% of the original amount of ligninsulphonate. In the presence of the chemical system, about 16% of the original ligninsulphonate remained in

the sample (Table VI).

The spectrum of the bath containing Blue 148 without the chemical system shows approximately 0.4% residual blue after treatment for 12 minutes. This was well within the limit set for residual dye after treatment, and experiments with this dyebath mixture were continued for this time. The treated bath was yellow, as evidenced by the height of the curve above the baseline between 400 and 440 nm.

In the UV region of the sample containing Blue 148 alone, peaks at 286 and 280 nm before and after treatment were used to calculate a residual ligninsulphonate content of about 7% (Table VI).

The treated bath containing Blue 148 and the chemical system was markedly yellow and slightly turbid after treatment. Six percent ligninsulphonate remained after treatment, calculated from the absorbances at 286 and 278 nm before and after treatment, respectively.

After treatment for 10 minutes, no color remained in the bath which contained Yellow 64 with or without the chemical system. Unlike the two other dyes used in this experiment, the commercial formulation of this dye contains large quantities of both ligninsulphonate and naphthalene sulphonate, both of which absorb at 280 nm.

In the bath without chemicals, there was only about 3% of the dispersing agent(s) remaining after treatment. Similarly, in the bath with chemicals, about 2% of the dispersing agent(s) remained (Table VI).

If the chemical system has any effect at all on electrochemical treatment of disperse dyebaths using aluminum electrodes, it is in retarding the removal of ligninsulphonate dispersing agent.

● Experiment 4: Effect of Electrochemical Treatment on Chemical Structure of Colorant in Disperse Dyes. The precipitate remaining on the filter paper following electrochemical treatment of 0.025% dispersions (containing the chemical system) of Red 263, Blue 148 and Yellow 64 for the optimal treatment times established in Experiment 1 was collected. It was solubilized in methylene chloride, spotted on a silica gel thin layer chromatography (TLC) plate and eluted with toluene and acetone in a 4:1 ratio. Comparison of the precipitate formed by the electrochemical treatment with the individual untreated dyes (containing the chemical system) showed that the dye structures were chemically identical. The TLC procedure was sensitive to detection of the colorant within the dye, and not to the dye auxiliaries or the dyebath assistants. Although we were able to evaluate the chemical nature of only the colorant after treatment, the result is consistent with the hypothesis that chemical degradation does not occur and physical adsorption is the major (the only?) mechanism of

effluent separation by electrochemical treatment with aluminum electrodes.

The integrity of the three colorants after treatment is contradictory to the results of dye degradation reported by McClung et al. (19). It is reasonable to assume that the difference is a result of the choice of electrodes in the two studies. Iron electrodes, as used by McClung, cause the release of ferrous iron which may act as a reducing agent to degrade the dye. In contrast, aluminum electrodes release aluminum which cannot act as a reducing agent since it enters solution in a single valence state.

Separation of effluent using aluminum electrodes may allow for the recovery of recyclable dye.

● Experiment 5: Effect of Treatment on Related Dye Structures. Dyes with similar structures should react in the same manner to electrochemical treatment. It would be reasonable to expect that a similar amount of aluminum would be needed to precipitate structurally similar colorants if present in comparable amounts in the commercial dye formulations.

In addition to the anthraquinone, azo and quinoline dyes used in previous experiments, a second dye of each chemical type and with known chemical structure was used in this experiment (Table I). Six dyebaths were prepared, with each containing 0.25% of one of the dyes as well as the chemical system. The baths containing

anthraquinone dyes as well as those containing the azo dyes were treated for 12 minutes, while those containing the quinoline dyes were treated for 10 minutes. The changes in the spectra of similar colorant structures were compared.

The two anthraquinone dyes—C.I. Disperse Red 263 and C.I. Disperse Blue 60—were difficult to compare because, although the amount of colorant was similar, a different combination of dispersing agents was used (Table I). The key peaks in the visible spectra of Red 263 and Blue 60 before treatment were no longer present after treatment.

The peaks in the UV region of Red 263 before treatment are not exact matches to those in the spectrum after treatment and hence quantitative comparisons are difficult. It does appear, however, that approximately 12% of the original amount of dispersing agents remained after treatment. The situation is similar with Blue 60 where an estimated 15% of the original mixture of dispersing agents was left in the treated effluent (Table VII).

C.I. Disperse Blue 148 and C.I. Disperse Orange 73, which contained comparable amounts of colorant and dispersing agent, are both azo dyes but differ markedly in substituent groups. The spectrum of the former dye prior to treatment showed the presence of an unidentified yellow component. The blue component of the dye was reduced to within our $\leq 2\%$ limit after a 12-minute treatment, while a

Table V. Removal of Dispersing Agents from Electrochemically Treated Baths Containing Dispersing Agent With and Without Crude Colorant

Dye	Dispersing Agent	Treatment Time	Residual Dispersing Agent
—	Naphthalene sulphonate, A	12 min	90%
—	Ligninsulphonate, B	12	88
—	Ligninsulphonate, C	12	82
C.I. Disperse Red 263	Ligninsulphonate	18	10
	Naphthalene sulphonate	24	14
C.I. Disperse Blue 148	Ligninsulphonate	18	9
	Naphthalene sulphonate	18	7
C.I. Disperse Yellow 64	Ligninsulphonate	10	17 ¹
	Naphthalene sulphonate	10	18

¹This sample contained both ligninsulphonate and naphthalene sulphonate dispersing agents—as in the commercial dye formulation—and the two could not be differentiated after treatment.

Table VI. Residual Dispersing Agent in Electrochemically Treated Baths Containing Commercial Dye With and Without Chemical System

Dye	Chemical System	Treatment Time	Residual Dispersing Agent
C.I. Disperse Red 263	no	12 min	6%
C.I. Disperse Red 263	yes	12	16
C.I. Disperse Blue 148	no	12	7
C.I. Disperse Blue 148	yes	12	6
C.I. Disperse Yellow 64	no	10	3 ¹
C.I. Disperse Yellow 64	yes	10	2 ¹

¹This sample contained both ligninsulphonate and naphthalene sulphonate dispersing agents, as in the commercial formulation, and the two could not be differentiated after treatment.

Analysis of Dyebath Effluent

small amount of the yellow component remained. The peaks in the visible spectrum of Orange 72, in contrast, were completely removed by the 12-minute treatment. It can be concluded, therefore, that the residual yellow in the former case is not due to the azo dye structure itself. As stated previously, we believe that either the sulfur based intermediates or byproducts of the dye synthesis gives rise to a yellow tinge in the treated sample which was not visible in the presence of the blue cloth.

The UV portion of the spectra showed that similar amounts of ligninsulphonate remained after treatment. Only 3.4% of the original amount of ligninsulphonate remained in Blue 148 after treatment compared to 2.6% in Orange 73 (Table VII).

Yellow 64 is a mixture which results from the bromination of C.I. Disperse Yellow 54. It consists of a variety of reaction products, all quinoline structures, one of which is Yellow 54. Examination of the formulations of the Yellow 64 and Yellow 54 reveals that the amount of colorant is considerably less, and the amount of dispersing agent considerably more, in the former than in the latter. Since the optimal treatment time was based on the commercial dye which contained the lower amount of colorant, and that optimal time decolorized the commercial product containing more colorant, it is likely that not only the colorant, but the colorant, dispersing agents and other ingredients in the commercial dye all have an effect.

In Yellow 64, a peak at 276 nm prior to treatment indicated the presence of dispersing agent(s). After treatment, the

Table VII. Residual Dispersing Agent in Baths Containing Dyes of Related Structures following Electrochemical Treatment

Dye	Treatment Time	Residual Dispersing Agent
C.I. Disperse Red 263	12 min	12% ¹
C.I. Disperse Blue 60	12	15 ¹
C.I. Disperse Blue 148	12	3.4
C.I. Disperse Orange 73	12	2.6
C.I. Disperse Yellow 64	10	0.7 ²
C.I. Disperse Yellow 54	10	0.9 ²

¹Estimate. ²This sample contained both ligninsulphonate and naphthalene sulphonate dispersing agents, as in the commercial formulation, and the two could not be differentiated after treatment.

amount remaining was 0.7%. The amount in the closely related Yellow 54 was calculated in the same manner to be 0.9% (Table VII). These samples contained both ligninsulphonate and naphthalene sulphonate and the two could not be differentiated after treatment.

The results of this experiment suggest that, when dyes with comparable structures are subjected to electrochemical treatment, they behave in a similar manner. The quinoline dyes appear to be the easiest of the three chemical types of disperse dyes to decolorize.

• Experiment 6: Validation of Model using Effluent from Laboratory Dyeings. Laboratory dyeings of 0.5%, 1.0% and 2.0% owf were done on five-gram samples of Dacron T-56 in a bath with a liquor ratio of 32:1 which contained the chemical system and Red 263, Blue 148 or Yellow 64 (for a total of nine dyeings). Blank dyeings containing fabric and the chemical system in water were also run to shed further light on the effect of these components in the dyebath.

The dyeings were done, in an Ahiba

Polymat, in accordance with the dyeing cycle illustrated in Fig. 7. The effluent generated from dyeings using the three concentrations of the same dye were combined to obtain the 500 mL needed for a single electrochemical treatment. The three resultant effluent baths were treated for the optimal times determined previously; i.e., 12 minutes for Red 263 and Blue 148, and 10 minutes for Yellow 64.

Since effluents always contain several dyes, dyeings were also done using a three-dye combination. Equal amounts of 0.1% Red 263, Blue 148 and Yellow 64 were combined to give a 2% owf dyeing. Three dyeings of each were done as before. Treatment time for the exhausted dyebath was estimated at six minutes.

The dilution required to obtain spectral peaks on the blank dyeing containing fabric and chemicals was markedly higher than that needed to obtain the peaks on the samples after dyeing or after electrochemical treatment. This affected the size and shape of the peaks throughout the spectrum, making comparison of these spectra very difficult. Nevertheless an estimated 69% of the chemical system which was present in the dyebath effluent remained after treatment.

The visible spectra of the Red 263 effluent showed that the peak which had been present at 518 nm before treatment was nonexistent after treatment, indicating total color removal. A peak appeared at 282 nm after treatment (ligninsulphonate) which was likely masked by the broad curve of the spectrum prior to treatment. Therefore, as in the previous experiments, while the effluent appeared to be pure water, in fact it contained a small amount of residual chemical and lignin.

The visible spectrum of the Blue 148 effluent after treatment showed total removal of the peak which had existed at 604 nm prior to treatment. The treated effluent was obviously yellow, as evidenced by peaks between 410 and 445 nm. The peak at 282 nm after treatment was hidden by the broad curve in this area of the UV region before treatment, making calcula-

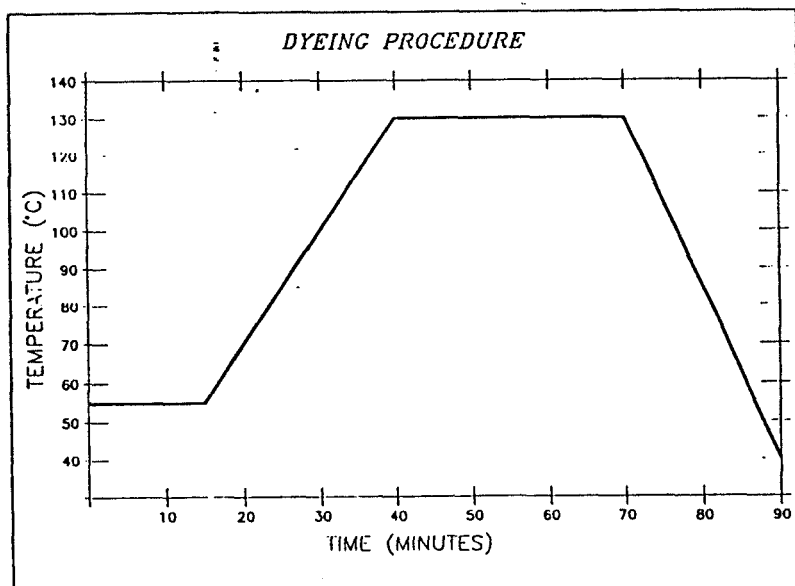


Fig. 7. Illustration of the dyeing cycle.

tion of residual dispersing agent impossible.

The effluent from the Yellow 64 effluent before treatment showed the presence of color between 400 and 440 nm as well as a small amount of turbidity. The color was totally removed by the treatment but the turbidity was not. In the UV region, the peak attributed to dispersing agent was reduced by 82% after treatment.

The spectrum from the mixture of Red 263, Blue 148 and Yellow 64 before dyeing showed the presence of red, blue and yellow peaks which were directly attributable to the component dyes. After dyeing, apart from a small peak at 428 nm, individual peaks were no longer distinct but existed as a curve parallel to the horizontal axis. This was interpreted to be gray color and/or turbidity.

In the UV portion of the spectra, a peak at 228 nm, indicating ligninsulphonate, was reduced by 26% during dyeing. The peak was reduced by an additional 81% by the electrochemical treatment.

Summary

Increasing treatment times, corresponding to increasing release of aluminum from the electrodes, caused increased removal of color from the disperse dyes examined. Regardless of the length of electrochemical treatment, it appears that not all the dye auxiliaries/dyebath assistants are removed from simulated dyebath effluents. The treated liquor cannot be considered to be water.

The presence of colorant in a dyebath facilitates the removal of dispersing agent. Compared to the naphthalene sulphonate type, ligninsulphonate dispersing agents appear to be more easily and completely removed from disperse dyes by electrochemical treatment with aluminum electrodes. Dyebath additives have either no effect, or a retarding effect, on the removal of ligninsulphonate dispersing agents. Whether this is of concern or not depends on the ultimate disposition of the treated effluent.

The electrochemical treatment did not cause degradation of Red 263, Blue 148 or Yellow 64. Therefore the dye removal process was one of physical adsorption and not dye destruction. Additional work on a larger number of dyes is necessary before this conclusion can be generalized to all disperse anthraquinone, azo and quinoline dyes.

In general, dyes with comparable structures reacted in a similar manner to electrochemical treatment. The quinoline dyes appear to be easier to decolorize than either the anthraquinone or azo dyes. The results suggest that not only the colorant but also the dispersing agents and possibly other components of the commercial dye formulation influence the efficacy of treatment.

The dispersing agents which were not

completely removed from simulated dyebath were also not completely removed from actual industrial dyebath effluent.

Conclusions

Spectrophotometric analysis shows that electrochemical treatment of disperse dyebaths with aluminum electrodes causes the removal of color, dispersing agents and dyebath assistants to variable degrees of completeness. At the time established for optimal color removal, the treated bath is not pure water. However, the contaminant content is low and the effluent could probably be reused "as is" in noncritical applications. Electrochemical treatment using aluminum electrodes is a viable method of cleaning up effluent for reuse.

Committee Members

The paper was presented by Anne Wilcock of the University of Guelph who also chaired the Hudson-Mohawk Section's ITPC research committee. Also on the committee were Jacqueline Tebbens, University of Guelph; Frank Fuss, Westvaco Corp. (formerly with BASF Corp.); John Wagner, BASF Corp.; and Michael Brewster, Andco Environmental Processes.

Acknowledgements

The committee would like to thank the following BASF personnel for their support during the course of experimentation: Paul Durante, Valerie Landrio, Karsanbhai Mistry and Leander Ricard. We acknowledge with thanks the cheerful co-operation of Rita Raso, University of Guelph, throughout the course of manuscript preparation. The financial support provided by Malden Mills Industries Inc. is also most appreciated.

References

- (1) Halliday, P. J. and S. Beszedits, *Canadian Textile Journal*, Vol. 103, No. 4, April 1986, p78.
- (2) Allen, W. et al., *Textile Chemist and Colorist*, Vol. 4, No. 12, December 1972, p275.
- (3) Durig, G., J. P. Hausmann and B. J. O'Hare, *Journal of the Society of Dyers and Colourists*, Vol. 94, No. 8, August 1978, p331.
- (4) Porter, J. J., *Water and Wastes Engineering*, Vol. 9, No. 1, January 1972, pA8.
- (5) Tincher, W. C., *Textile Chemist and Colorist*, Vol. 21, No. 12, December 1989, p33.
- (6) EEC International Environmental Consultants Ltd., *Survey of Textile Wet Processing and Pollution Abatement Technology*, Environment Canada (publishers), 1982.
- (7) Smith, B., *Identification and Reduction of Pollution Sources in Textile Wet Processing*, Pollution Prevention Program, Raleigh, N. C.
- (8) Cook, F., R. M. Moore and G. S. Green, *Textile Chemist and Colorist*, Vol. 21, No. 4, April 1989, p11.
- (9) Cook, F. L. et al., *Textile Chemist and Colorist*, Vol. 12, No. 1, January 1980, p15.
- (10) Cook, F. L. and W. C. Tincher, *Textile Chemist and Colorist*, Vol. 10, No. 1, January 1978, p21.
- (11) Porter, J. J., *American Dyestuff Reporter*, Vol. 62, No. 4, April 1973, p21.
- (12) Shriver, L. E. and R. R. Daugue, *American Dyestuff Reporter*, Vol. 67, No. 3, March 1978, p34.
- (13) Tincher, W. C., F. L. Cook and L. A. Barch,

Textile Chemist and Colorist, Vol. 13, No. 12, December 1981, p14.

(14) Wilcock, A. and S. Hay, *Canadian Textile Journal*, Vol. 108, No. 4, May 1991, p37.

(15) Reife, A., *Book of Papers, 1989 AATCC International Conference & Exhibition*, Philadelphia, p320.

(16) Rodman, C. A., *Textile Chemist and Colorist*, Vol. 3, No. 11, November 1971, p45.

(17) Uhrich, K. D. and T. R. Demmin, *Book of Papers, 1988 AATCC International Conference & Exhibition*, Nashville, p97.

(18) Kennody, M., *American Dyestuff Reporter*, Vol. 80, No. 9, September 1991, p26.

(19) McClung, S. and A. Lemley, *Electrochemical Treatment of Acid Dye Wastewater*, Preprint Extended Abstract, American Chemical Society Division of Environmental Chemistry, Washington, D. C., August 23, 1992.

(20) Tincher, W. C., M. Weinberg and S. Stephens, *Book of Papers, 1988 AATCC International Conference and Exhibition*, Nashville, p25.

(21) Weinberg, M. K., *The Effectiveness of the Andco Electrochemical Treatment Process and Its Application in Textile Wastewater Treatment*, Georgia Institute of Technology, MS Thesis, August 1989.

(22) Demmin, T. and K. D. Uhrich, *American Dyestuff Reporter*, Vol. 77, No. 6, June 1988, p13.

(23) Jones, D. L., *American Dyestuff Reporter*, Vol. 61, No. 8, August 1972, p28.

(24) Wilcock, A., M. Brewster and W. Tincher, *American Dyestuff Reporter*, Vol. 81, No. 8, August 1992, p15.



How's Your Laboratory Detergent Supply?

AATCC Detergent 124

Used for testing smoothness appearance, dimensional changes in home laundering and soil release. 50 lb. container \$110 plus shipping & handling. Order No. 8351

AATCC Detergent WOB

Without optical brightener, used in testing colorfastness to washing. 20 lb. bucket \$60 plus shipping & handling. Order No. 8352

AATCC Detergent 171

Used for AATCC TM 171 — simulated floor cleaning by hot water extraction method. 20 lb. bucket \$60 plus shipping & handling. Order No. 8722

AATCC

P.O. Box 12215

Research Triangle Park, NC 27709

Tel: 919/549-8141

Fax: 919/549-8933

VISA OR MASTERCARD ACCEPTED

