Knob-Twiddling to Answer Questions about Textile Wet Processing Chemicals and Processes

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INTRODUCTION

Behind the colors and functions of textile materials that we use in everyday life lies a tremendous amount of chemistry. To develop dyeing and finishing chemicals and to improve the processes by which they are applied, it is necessary to analyze those materials. Such analyses involve many different instrumental techniques. In this paper, the focus will be primarily on spectroscopy (i.e., nuclear magnetic resonance (NMR), mass spectrometry (MS), near infrared (NIR), and ultraviolet-visible (UV-Vis) spectroscopy) and chromatography (i.e., gas chromatography (GC) and high-performance liquid chromatography (HPLC)). Before computers were developed and adapted to control these instruments, many of the adjustments were made by turning knobs. Over the past 35 years, the power of these instruments to answer textile wet-processing questions (e.g., "What is it?" and "How much of it is there?") has increased tremendously. With data answering these fundamental questions, it is possible to improve textile wet processes and chemicals. Examples of some of these knob-twiddling investigations are given in this paper with a focus on durable-press finishing and dyebath monitoring.

NIR SPECTROSCOPY

NIR spectroscopy is an excellent tool for answering both qualitative and quantitative questions, especially for fiber identification and blend analysis. It is a non-destructive secondary analytical technique (i.e., the instrument must be trained using data from a primary technique, which requires little or no sample preparation.) Howell and Davis[1] developed a simple NIR library that could be used to identify cotton, rayon, nylon, polyester, acrylic, polypropylene, and wool fibers. Those seven classes of fibers were expanded to include acetate, modacrylic, poly(vinyl alcohol), poly(vinyl chloride), silk, triacetate, *para*-aramid (Kevlar), and *meta*-aramid (Nomex).[2] Cotton was not differentiated from linen and nylon fibers could not be classified according to dyeability in this study. It was, however, possible to differentiate among the 29, 49, and 129 grades of Kevlar by NIR.

Very early work by Tincher and Luk showed that NIR was an excellent tool for analysis of polyester/cotton blends in yarns.[3] In recent AATCC committee work, we have revisited this question: calibration models were developed from a training set of 265 polyester/cotton fabrics and those models were validated by predicting the percent polyester in 35 fabrics of known composition.[4] The NIR-lab polyester content results agreed to within ±5.0% for over 90% of the validation samples. The use of second derivative spectra and standard normal variate (SNV) normalization minimized the impact of baseline effects and of fabric color and patterns.

CARBON DIOXIDE: SOLVENT AND PROCESSING FLUID

Another "How much?" question was answered using supercritical carbon dioxide (CO_2). For many years, the amount of organic-soluble matter in greige fabrics was determined by Soxhlet extraction into 1,1,1-trichloroethane (TCE).[5] Using supercritical CO_2 at various pressures and temperatures, the wax content of greige cotton fabrics was determined.[6] The goal of this particular work was to develop an extraction method that did not use a halogenated solvent. We found that a small amount of ethanol acted either as a co-solvent for the wax or disrupted the hydrogen bonds in the cotton cellulose; all of the wax could be removed by supercritical CO_2 extraction with an efficiency comparable to TCE Soxhlet extraction.

As is often the case in science, experience with the supercritical fluid extractor led to its reconfiguration to help us answer questions for another project. Exhaust dyeing of polyester in water is typically effected at 130C with disperse dyes. As part of a large project to determine if polyester could be technically and economically dyed in supercritical CO_2, it was necessary to determine two important characteristics of disperse dyes: their solubility as a function of temperature and pressure,

ABSTRACT

For three decades, we have used analytical instruments to investigate important chemicals and their effects in textile wet processing. High-performance liquid chromatography (HPLC), gas chromatography/mass spectrometry (GC/MS), and C^{13}-NMR (carbon-13 nuclear magnetic resonance) spectroscopy provided valuable information about durable press reagent composition and effects in the bath and on the fabric. We used liquid CO_2 as a dry cleaning solvent and supercritical CO_2 for extraction of waxes from cotton and for dyeing polyester. To monitor dye exhaustion, we developed direct dyebath monitoring, flow injection analysis (FIA), and sequential injection analysis (SIA) systems. Coupling FIA and HPLC allowed us to simultaneously monitor exhaustion and hydrolysis of reactive dyes in real time. This paper will address three questions: "What is it?" "How much is there?" and "What is happening to it in the process?"

Key Terms

Analysis
Dyeing
Instrumentation
Processing

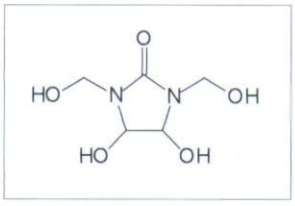

Fig. 1. Structure of DMDHEU.

and their affinity for polyester in supercritical CO_2. Using a modified supercritical fluid extractor, we measured the solubility behavior of several disperse dyes.[7] This information was critical in designing a dyeing process that prevented surface deposition of the dye during depressurization.

In the late 1990s, there was tremendous interest in developing alternatives to perchloroethylene as a drycleaning solvent. Cleaning processes involving liquid CO_2 were being developed. Little was known about the fastness properties of dyes in CO_2. Samples of commonly drycleaned fabrics (triacetate, acetate, silk, rayon, polyester, and wool), each dyed with 10 different dyes, were prepared and subjected to liquid CO_2 in a laboratory machine, a pilot-scale CO_2 cleaning machine in Germany, and in a commercial CO_2 drycleaning machine. Results indicated that all of the dyed fabrics except triacetate exhibited good fastness (DE < 1) in the commercial machine.[8]

DURABLE PRESS FINISHING

In the mid-1960s, durable press (DP) finishing was significantly improved by the introduction of dimethyloldihydroxyethyleneurea (DMDHEU, Fig. 1). DMDHEU was still the dominant DP finish in the late 1970s and early 1980s. Intensive research and development efforts were made to reduce the amount of formaldehyde released by finished fabrics. The next section of this paper relates some of our efforts to better understand the structures and the properties of DMDHEU finishes and some related methylol compounds. Much of this research was supported by and conducted in collaboration with a group of researchers at the U.S. Department of Agriculture (Southern Regional Research Center).

Early HPLC Analysis of DP Agents

Because DMDHEU (Fig. 1) is very polar and contains hydroxyl groups, our early attempts to analyze it by HPLC were based on methods used to analyze carbohydrates.[9] The columns were water-jacketed 8 mm x 410 mm tubes self-packed with the Li^+ form of a cation exchange resin (6% sulfonated divinyl benzene crosslinked polystyrene). These columns were typically thermostated at 60C-70C and run at 0.5 mL/min with water as the mobile phase. As indicated by their plate counts of 4,000-6,000 plates/m, the columns were not very efficient, but they were useful for monitoring the synthesis of DP agents and measuring them in extracts of finished fabrics and in commercial finishing products.

To study the acid-catalyzed crosslinking reaction between DMDHEU and cellulose, fabric was padded with in-house prepared DMDHEU and $MgCl_2$, dried to minimize migration, and cured at different temperatures. The partially-cured fabrics were extracted with water and the resulting extract quantitated by HPLC.[10] From the initial concentration (C_0) and the concentration (C) at various times (t) at each temperature, the rate constant for crosslinking was calculated using $\ln(C_0/C) = kt$. A plot of $\ln(C_0/C)$ vs. t gave a straight line indicating a pseudo first-order reaction. When ln k was plotted against $1/T$, where T is the absolute temperature, the energy of activation (E_{act}) was found to be 29.2 kcal/mol. This compared very favorably with the literature value of 29.4 kcal/mol.[11]

In a subsequent study, HPLC was used to determine the effect of pad-bath pH and storage on the hydrolysis of DMDHEU.[12] It was found that DMDHEU padded on fabric and dried but not cured was stable for up to 55 days as long as the pH did not exceed 6. Above pH 6, hydrolysis occurred within one day of application. At pH 10, the maximum amount of monomethyloldihydroxyethyleneurea (MMDHEU) was generated after one day and hydrolysis to dihydroxyethyleneurea (DHEU) was complete between 15 and 55 days. It was obvious that the pH of the pad-bath is more important than the storage period in the production of post-cured fabrics.

A similar study with dimethylolethyleneurea (DMEU) was performed with a 70/30 water-methanol solvent-conditioned C18 reverse phase HPLC column using water as the mobile phase.[13] It was found that DMEU, as expected, was much less stable on fabric than DMDHEU. After 15 days, only 18% of the original DMEU, compared to 86% for DMDHEU, remained on the fabric padded with a pH 6 bath. DMEU also formed oligomers by reaction with itself.

Removal of DMDHEU Crosslinks

It is well known that cotton cellulose is significantly weaker after crosslinking due to DP treatment than before DP treatment. One possible explanation is a decrease in the degree of polymerization (dp) during the acid-catalyzed DP-finishing process. To determine the dp of the finished cellulose, the crosslinks must be removed so the cellulose can be dissolved. Realizing that cellulose is stable to mercerizing-strength NaOH, we found that boiling DMDHEU-crosslinked cotton fabric in 23% NaOH under nitrogen for 10 min removed all crosslinks.[14] Table I shows some of the chemical and physical properties of the control fabric (unfinished but treated with NaOH), fabrics finished with DMDHEU/$MgCl_2$ (Sample A), and fabrics finished

TABLE I.

Properties of Control, Finished, and Stripped Fabrics

	Breaking Load (N)	WRA (W+F)[a] (°)	%Nitrogen	%CH_2O	dp_v
Control	272	194	~0.0	~0.0	3,720
DMDHEU + $MgCl_2$ (A)	135	286	1.1	2.95	—
A Stripped	249	194	~0.0	~0.0	2,820
DMDHEU + $MgCl_2$ + CA[b] (B)	156	272	1.06	2.83	—
B Stripped	274	185	~0.0	~0.0	3,050

[a]WRA (W+F) stands for Wrinkle Recovery Angle (Warp and Fill).
[b]Citric acid.

TABLE II.

^{13}C-NMR Chemical Shifts[a]

Carbon Atom	Chemical Shift (ppm)	Carbon Atom	Chemical Shift (ppm)
$\underline{C}HOH$ (trans)	~86	$\underline{C}HOCH_3$ (trans)	~91
$\underline{C}HOH$ (cis)	~80	$\underline{C}HOCH_3$ (cis)	~88
$\underline{C}H_2OH$	~66	$CH_2\underline{O}CH_3$	~57
$\underline{C}H_2OCH_3$	~75	$CHO\underline{C}H_3$	~56

[a]The carbon atom for which the chemical shift was determined is underlined.

with DMDHEU/$MgCl_2$ + citric acid (Sample B).[15]

The data showed that some, but not all, of the decrease in strength caused by DP finishing is caused by a decrease in dp (as determined by viscosity). The major portion of the strength loss is probably due to the localization of tensile forces in the crosslinked cellulose.

Characterization of Commercial DP Finishes

In the 1980s, major emphasis was placed on lowering the amount of formaldehyde released by fabrics finished with DMDHEU. One way to effectively lower the formaldehyde released was to convert some of the hemiacetal hydroxyls in DMDHEU to acetals by reaction with an alcohol. In an extensive study, a combination of HPLC,[16] GC/MS,[17] and carbon-13 NMR (^{13}C-NMR)[18] was used to elucidate structures of the many components in methylated and glycolated (diethylene glycol) DMDHEU finishes. To analyze the DP agents by GC/MS, the components were converted to trimethylsilyl derivatives by the reaction shown in Fig. 2. Fig. 3 shows the identified products formed when DMDHEU is alkylated with methanol. Fig. 4 shows the structures of the identified components of a commercial glycolated DMDHEU finish. Table II shows the ^{13}C-NMR chemical shifts of carbons that were important in identifying structures of the methyl ethers of DMDHEU.[18] A summary of chromatographic and spectroscopic methods for analyzing DP agents has been published.[19]

DYEBATH MONITORING

In 1988, three textile chemistry faculty and two engineers at North Carolina State University began a dyebath monitoring and control project that evolved into the Dye Applications Research Group. Our goal was to develop dyebath monitoring capabilities that would allow control of the exhaust dyeing process so that every dyeing would deliver the correct shade. The summary given here will focus only on the monitoring portion of this project. Brent Smith and I have been involved in this project since its inception. Warren Jasper joined the project in 1991. None of the following work would have been possible without the significant contributions of these two colleagues.

Direct Dyebath Monitoring

Our first monitoring system was based on a fixed path-length fiber optics spectrophotometer.[20] This was a valuable research tool that allowed us to monitor dyeings with water-soluble

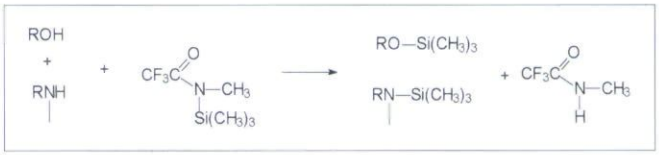

Fig. 2. Silylation of reactive OH and NH groups in DP agents.

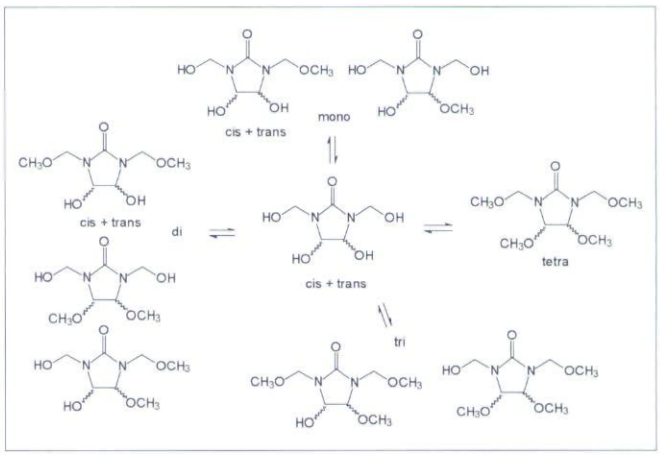

Fig. 3. Identified structures for methylated DMDHEU.

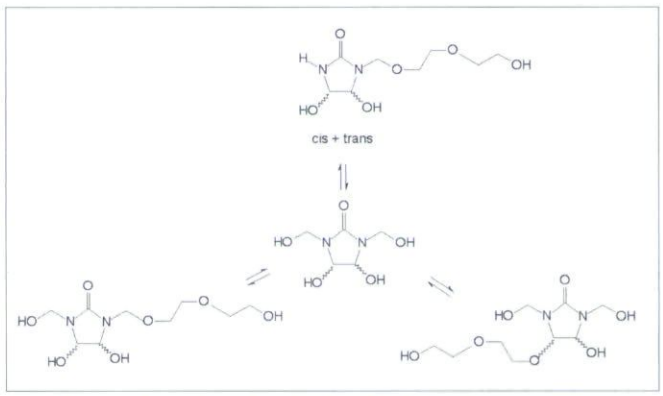

Fig. 4. Identified structures for glycolated DMDHEU.

dyes, but the dynamic range of dye concentrations that could be measured was limited by the fixed path-length. The direct dyebath monitoring system could not compensate for changes in dyebath pH which might cause changes in dye structures and spectral characteristics. Even with the above limitations, the system allowed us to study many variables and to develop control systems that closed the loop in the dyeing process.

Flow Injection Analysis

To overcome the limitations of the direct dyebath monitoring system, we developed a flow injection analysis (FIA) system. A schematic diagram of the system is shown in Fig. 5.

In FIA, a small volume of dyebath is injected into a flowing stream of appropriate solvent carrier and passed through a mixing chamber where controlled and precise dilution occurs. The plug of diluted dyebath then passes through a flow cell where UV-Vis spectra are taken at very short intervals. A calibration model is applied to an individual spectrum from a specific time slice to generate the concentration of up to three dyes. Since this analytical process can be completed in about

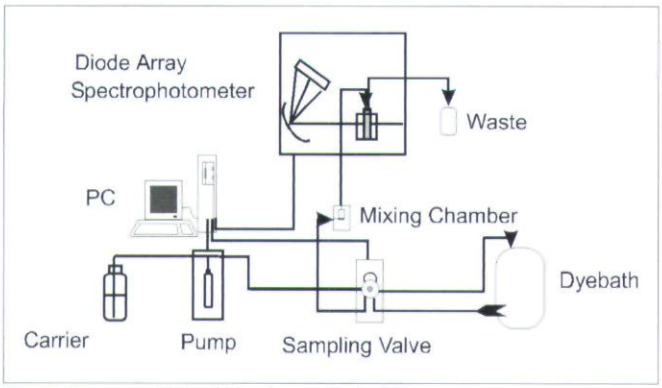

Fig. 5. Diagram of flow injection analysis (FIA) system.

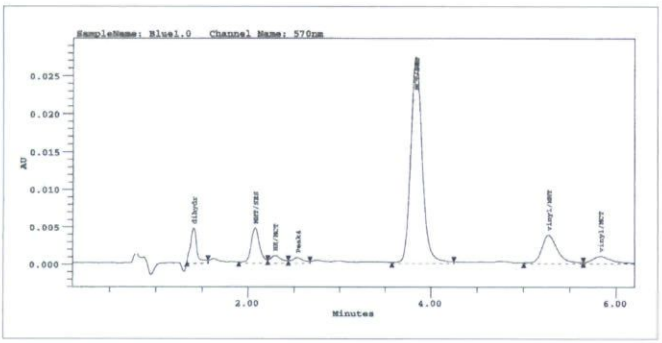

Fig. 7. HPLC chromatogram of a heterobifunctional reactive blue dye.

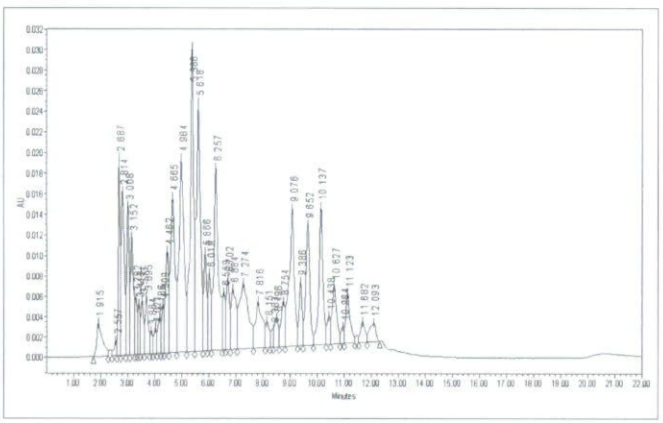

Fig. 9. Optimized chromatogram of C.I. Reactive Blue 21.

one minute, conversion of dye concentration to percent exhaustion leads to real-time information about the movement of dye from the bath to and from the fiber surface.

FIA has been used to determine the exhaustion of reactive,[21] direct,[22] indigo,[23] sulfur,[24] acid,[25] and disperse[26] dyes. Fig. 6 shows typical exhaustion curves for three disperse dyes on polyester. This dyebath monitoring work has been summarized in a recent publication.[27] Much of this work has led to an increased understanding of the fundamental kinetics and thermodynamics of the dyeing process and to answering questions concerning dyeing problems.

Sequential Injection Analysis

In FIA, the sample size is determined by the volume of the loop on the valve. To change the volume of the dyebath, the

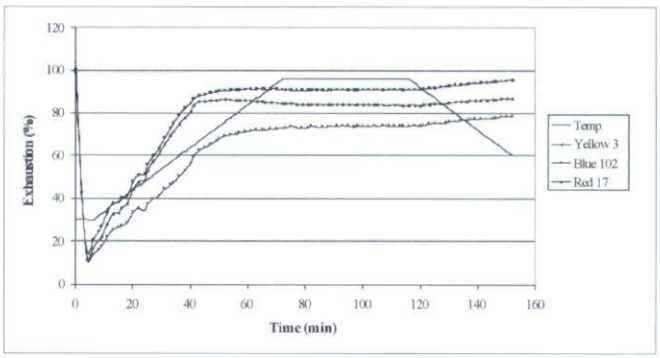

Fig. 6. FIA exhaustion curves for three high energy disperse dyes on PET.

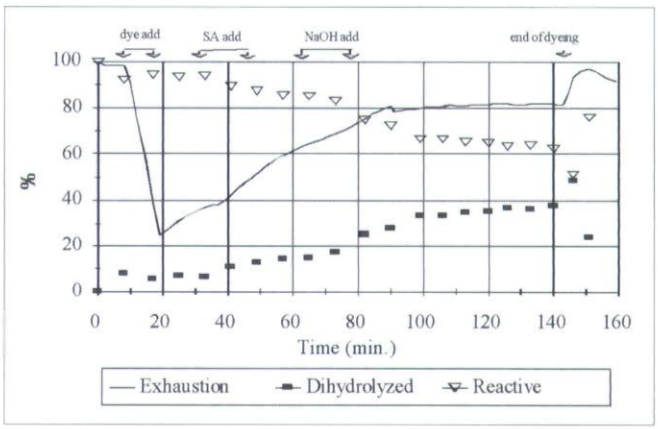

Fig. 8. Plot of exhaustion and hydrolysis of a reactive blue dye.

loop must be physically changed. To make the sample volume variable, we developed a sequential injection analysis (SIA) system.[28] In addition to changes in the control software, the SIA system hardware included a sample coil into which a variable volume of the dyebath was drawn. The 6-port FIA valve was replaced by a 10-port valve. The precision and accuracy of the SIA system was not significantly different from the FIA system, but SIA has the advantage of handling a variable sample volume.

FIA/HPLC

FIA has been used extensively to monitor the exhaustion of dyes, but it can not measure the extent of hydrolysis of a reactive dye because the visible spectrum of a hydrolyzed form of the dye is not significantly different from the visible spectrum of the reactive form. To overcome this limitation, we coupled the FIA system with an HPLC equipped with a diode array detector.[29] The waste from the FIA flow cell was passed through a high-pressure six-port valve that was connected to a reverse phase HPLC column. This FIA/HPLC system allowed the simultaneous determination of reactive dye exhaustion and hydrolysis. A chromatogram of a blue heterobifunctional (monochlorotriazine and sulfatoethylsulfone) reactive dye is shown in Fig. 7. Fig. 8 shows dye exhaustion and hydrolysis as a function of time.

Because of the importance of HPLC as a tool for analyzing the hydrolysis of reactive dyes, we recently developed improved methods for these analyses.[30] Fig. 9 shows an optimized chro-

matogram of C.I. Reactive Blue 21, a complex sulfonated phthalocyanine dye containing at least 43 blue components.

CONCLUSIONS

Over the past three decades, our ability to analyze chemicals in textile processes has dramatically increased. We are able to analyze materials faster and more completely than ever before to provide a body of new knowledge to improve and create textile wet processes. Information provided here on durable press agents and dyebath analysis is a trickle from the river of data flowing from research laboratories.

Acknowledgements

Support for this work was received from the U.S. Department of Agriculture (Southern Regional Research Center), the National Textile Center, the Consortium for Research in Fibers, Textiles and Manufacturing, the Environmental Protection Agency, Purdue University, and North Carolina State University. In addition to many faculty, industrial, and government colleagues who contributed significantly to the research mentioned here, the following students and research associates who so ably performed the work are gratefully acknowledged: Dilip Pasad, Karen Springer, Prashant Abhyankar, Martin Wusik, Beverly Leibowitz, SuChul Chung, Rosemary Kunz, Herbert Kulube, Tod Madderra, Jennifer Williams, Michele Wallace, Sara Draper, Rachel Slivensky, Jay Merritt, Tatjana van Delden, Bill Snyder, Gordon Berkstresser, Gerardo Monterro, Tracey Marlowe, Jana Lykins Wharton, Lynn Grady Moore, Andy Monfalcone, and Cindy Salley. Recognition for this work should be shared with each of them. Figs. 5, 7, 8, and 9 are reproduced with the permission of AATCC.

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