

**UNION DYEING COTTON/WOOL BLENDED
FABRICS: EFFICIENT
PRETREATMENT/DYEING PRESCRIPTIONS**

**J. M. Cardamone, E. Piotrowski,
A. Francis and W. N. Marmer
USDA, ARS**

**Eastern Regional Research Center
Wyndmoor, PA**

Abstract

Blended textiles of wool and cotton are conventionally dyed to one uniform shade in one or two dyebaths with one or two dyes where the different fiber types are dyed sequentially in two steps, under different requirements for alkalinity/ acidity and temperature. This cumbersome process has now been simplified to a one-step dyeing process with one dye. The new process relies on the selective modification of the cotton component in the presence of wool in a pretreatment step to dyeing, followed by dyeing from a fresh dyebath with a wool or cotton dye. The pretreatment compounds are commercially available dye fixatives that impart cationic character and polyamino functionality to cotton cellulose. These compounds vary in their ability to convey union dyeing behavior to wool/cotton blends. The new pretreatment/ union dyeing systems are dependent on processing conditions for the quality of union shade. Dye fixatives of various functions were used with various dye classes to determine the optimum conditions for achieving union shades of high color strength and colorfastness. The most effective pretreatment/union dyeing system was found to be pretreatment with a poly(diethylenetriaminebiguanide) (PDETAB) compound, followed by dyeing with a wool reactive dye with alpha-bromoacrylamido functionality. This report describes the effectiveness of PDETAB in promoting union dyeing of wool/cotton blended fabrics, including cross-wovens (interlacing wool and cotton yarns), intimate yarn blended fabric of wool and cotton, and wool and cotton fibers before blending.

Introduction

In earlier studies we adopted the technology of *dyeable* durable-press (DP) cotton that was developed at the Southern Regional Research Center (SRRC). This technology involved the co-addition of amine compounds to pad application baths containing the DP resin, dimethyloldihydroxyetheneleurea (DMDHEU). We applied resin systems by the co-addition of a low- or a non-formaldehyde resin, with ethanolamine (MEA) by pad-dry-cure, to a cross-woven fabric of 62% wool and 38% cotton. The fabrics were dyed subsequently with reactive wool dyes having alpha-bromoacrylamido reactive groups for chemical

bonding to the aminized cotton portion of the fabric. Dyebaths exhausted completely, leading to union dyed fabrics with high color strength and the excellent colorfastness suitable for textile products that could be home-laundered.

In cooperative research with SRRC laboratory, we carried out parallel studies on pretreatment systems containing DMDHEU resins and choline chloride (CC), a cationic amine compound, to cationize the cotton portion of the cross-weave fabric. The cationized cotton then dyed competitively in the presence of the wool to union shade in acidic dyebath medium with acid and direct dyes. We obtained union-dyed blends of high color strength which matched the depth of shade of unpretreated and pretreated wool dyed with the same dyes. We concluded that wool was essentially unaffected by the DMDHEU/CC pretreatment. In the case of the cotton component of the blend, it was essentially undyed without this pretreatment. The DMDHEU/CC pretreatment led to high color strength which was comparable to the color strength of the wool component when dyed alone. The DMDHEU/CC system provided union shades with excellent colorfastness to wet and dry crocking, drycleaning, and light exposure. However, colorfastness to laundering was poor. These fabrics would be suitable for outerwear and should be refurbished by drycleaning.

We then turned our attention to exhaust applications of certain commercial dye fixatives to pretreat wool/cotton blends for subsequent union dyeing. These compounds are derived from the condensation of polyamino compounds with compounds containing different functional moieties such as epichlorohydrin and epoxy azetidene. Although all of the fixatives selected proved to be effective for union dyeing the cross-woven fabric with an acid dye, the colorfastness to laundering and wet crocking of the union-dyed fabrics was poor. Thus, fabricated products for apparel must be restricted to outerwear and refurbishing by "dry-clean only."

When the epichlorohydrin and epoxy azetidinium fixatives were applied to wool/cotton blends for subsequent union dyeing with direct and wool reactive dyes, the color strengths of the dyed fabrics were lower than that of unpretreated *and* pretreated wool fabrics dyed with the same dyes to the same dyeing depth. Additionally, these union dyed blends exhibited poor colorfastness. However when the biguanide, PDETAB, was applied to 62% wool/ 38% cotton cross-woven fabric under application conditions: 20 grams/100 mL, three hours, pH 11, room temperature; the colorfastness of the fabric blends that were union dyed with wool reactive (alpha-bromoacrylamido) dyes exhibited excellent colorfastness properties, including colorfastness to wet crocking and laundering.

The PDETAB pretreatment/wool reactive dye system for union dyeing was then optimized for dyeing 62%wool/38% cotton crosswoven fabric.

In addition, knitted fabrics of an intimate yarn blend of 55% wool and 45% cotton and also wool and cotton fibers pretreated and dyed as fibers were examined. Optimum conditions that yielded high color strengths, dyebath exhaustions, and colorfastness were 4g/100mL PDETAB, applied from exhaust baths, at pH 6.5, for 45 minutes to one hour, at room temperature. In the case of the *intimately blended yarn fabrics*, there was little loss in color strength after 25 home laundering cycles. Under these optimum conditions, *wool and cotton fibers were pretreated separately, and then dyed separately or together* as a 55% / 45% fiber blend. Subsequent dyeings with a 2% (by weight of fabric) wool reactive dye processed at pH 5.5 to 6.5 and then processed at pH 7.0 to 8.0 for a 3% dyeing produced the same shade (union dyed) on both fiber types. In fact, at these depths of dyeing, union shades could be achieved whether the pretreated cotton fibers were with either pretreated or unpretreated wool fibers. However, in the case of 4% dyeings at pH 7.0 to 8.0, union shades were not obtained. The obvious 3% limitation suggested that the biguanide-pretreated cotton fibers could furnish only a limited number of dye sites.

Ensuing experiments led to establishing the optimum pretreatment conditions for applying PDETAB to 68% wool / 32% cotton cross-woven fabric for union dyeing with wool- reactive dyes containing alpha-bromoacrylamido functions and with cotton-reactive dyes containing vinyl sulfone functions. We established the following optimum pretreatment conditions: *exhaust applications*: 0.6 grams/100mL or 4 grams/100mL PDETAB, pH 6.5, 60C, 20 minutes; *padding applications*: 0.6 grams/100mL PDETAB, pH 6.5, 20C. Both modes of application produced the same high color strength in subsequent 3% dyeings. Fixative concentrations as low as 0.15g/100 mL, when applied by padding, were equally as effective with excellent colorfastness to laundering. However, colorfastness to wet crocking was poor, unlike the fabrics that were pretreated with 20 grams/100 mL PDETAB as noted above.

Our experience with PDETAB fixative/union dyeing systems leads us to hypothesize that PDETAB is firmly bound to cotton cellulose by the association of ionic charges and that it is the fixative that is actually dyed. The stability of the PDETAB-cellulose association can affect the colorfastness of the union dyed wool/cotton fabric. The association of PDETAB with cotton cellulose is an equilibrium reaction that requires excess PDETAB to form cationic cotton. We investigated the potential of reusing this excess for subsequent cationization of more fabric. We found that pretreatment baths constituted to concentrations of 4g/100mL and 2g/100mL could be reused up to six times to produce union dyed fabrics with high color strength only slightly lower than the pretreated fabrics from the original

pretreatment bath. The lowest recommended PDETAB concentration to apply *by exhaust* for union dyeing with wool reactive dye was 0.8g/100mL when applied at pH 6.5 for 60 minutes at 20C. The lowest recommended PDETAB concentration to apply *by padding* for union dyeing with wool reactive dye was 0.4g/100mL when applied at pH 6.5 by one dip and nip at 20C.

A broad palette for wool reactive dyes may not be as readily available as are those available for cotton reactive dyes. Therefore we investigated those cotton reactive dyes with vinyl sulfone functions. Like the wool reactive alpha-bromoacrylamido dyes, vinyl sulfone dyes process for reactive dyeing at relatively mild conditions of alkalinity. Thus in dyeing, they favor wool and like the wool reactive dyes, they also have the versatility of behaving like acid dyes when processed from acidic medium. The effectiveness of these cotton reactive dyes was studied in systems employing PDETAB biguanide as well as another fixative, poly(hexamethylene-biguanide) (PHMB; Zeneca Biocides, Wilmington, Delaware). Cationic PHMB was designed to cationize cellulose for antimicrobial efficacy. PDETAB and PHMB-pretreated wool/cotton blends were union dyed with mono- and bifunctional vinyl sulfone dyes. PDETAB proved more versatile for obtaining union shades with high color strength. However, colorfastness to wet crocking and laundering was poor. These colorfastness properties were not improved when PHMB replaced PDETAB in the system.

After the cotton cellulose in wool/cotton blended fabrics is cationized, it is reasonable to select for study the union dyeing system. *In this report*, we now present the results of our latest study on PDETAB pretreatment/ acid metallized dyes applied for the union dyeing of 62% wool/38% cotton cross-woven fabric.

Discussion

Effects of PDETAB Concentration and Exposure Time on Union Dyeing with Acid Metallized Dyes

All cotton and all wool fabrics were pretreated individually with PDETAB under two sets of conditions: 4g/100mL, pH 6.5, 60 minutes, 20C and 0.8g/100mL at pH 6.5, 15 minutes, 20C. First the pretreated wool and cotton fabrics were dyed individually. Next, another set of pretreated wool and cotton fabrics were dyed together. Color strengths were compared to color strengths of unpretreated *and* pretreated 62% wool/ 38% cotton cross-woven fabrics that were dyed similarly after PDETAB pretreatments as shown in Table 1.

From Table 1, PDETAB has a retarding effect on the dye uptake of wool, whether pretreated wool is dyed alone or in the presence of cotton. This retarding effect is most pronounced for Lanasyn Black S-GL and Lanasyn Grey S-BG. Under microscopic examination, PDETAB appeared to form a uniform, coating on the wool fibers. PDETAB,

acting as a dye-resisting agent, can contribute to poor colorfastness to laundering and wet crocking. Surface coating could retard dye uptake on pretreated wool/cotton fabrics. Note that their color strengths are closer to those of pretreated wool fabrics, whether these wool fabrics were dyed alone or in the presence of pretreated cotton. As intended, PDETAB-pretreated cotton fabrics exhibited improved dyeability, whether they were dyed alone or in the presence of pretreated wool fabrics. Except for the Intralan Navy SB (the only nonmetallized dye in the group) -dyed wool and cotton fabrics, there is little difference in their color strengths whether they were pretreated with 0.8g/100mL or at 4g/100mL PDETAB. From Table 1, the dyeings of pretreated wool fabrics and pretreated cotton fabrics did not exhibit synergism, for such would result in higher color strength values comparable to the unpretreated and dyed wool fabric samples.

Effects of Lanasyn Black S-GL Dye Concentration on the Union Dyeing of Cotton and Wool Fabrics Pretreated with 4g/100mL PDETAB

To further investigate the diminishing shade characteristics of wool fabrics pretreated with PDETAB, the percentage of Lanasyn Black S-GL dye was varied from 0% to 10% on cotton and wool fabrics pretreated individually with 4g/100mL PDETAB fixative at pH 6.5, for 60 minutes at room temperature for subsequent individual dyeings. The results shown in Graph 1, "Percent Dye vs. Color Strength," indicate that at a 5% concentration, pretreated wool and cotton fabrics reach approximately the same color strengths and above this concentration, union shade would be sacrificed because of cotton's increasing dye affinity over wool's. A maximum of 5% should not be exceeded if union shades are to be achieved.

Effects of PDETAB Concentration on the Union Dyeing of Cotton and Wool Fabrics with 10% Lanasyn Black S-GL

In order to determine if the system could be altered to attain higher color strengths, the concentration of PDETAB was varied from 0.1g/100mL to 20g/100mL and applied at pH 6.5 for one hour at 20C to wool and cotton fabrics before dyeing with 10% Lanasyn Black S-GL. The results shown in Graph 2, "Percent PDETAB vs. Color Strength," indicate that in the union dyeing of pretreated wool and cotton fabrics, a maximum % PDETAB of 0.4g/100mL is recommended for union shade; above this concentration, union shade would suffer in subsequent dyeings with 10% Lanasyn Black S-GL.

Summary

Commercial dye fixatives of biguanide functionality and certain similar cationic compounds with polyamino chain extensions are effective pretreatment compounds for modifying cotton cellulose with cationic charge. The formation of cationic cotton opens the possibility of union dyeing wool/cotton blended fabrics from one dyebath, with

only one dye, provided the wool and modified cotton constituents exhibit equal affinities and substantivities for the dye. We have found that this one-step union dyeing process is specific to the textile substrate, as well as fixative and dye used, and processing applications. *At the pretreatment stage*, it is recommended that experiments be carried out to vary fixative concentration, pH, exposure time, and application temperature for fractional factorial analysis to determine the optimum set of conditions for pretreatment fixation. *At the dyeing stage*, we recommend comparative preliminary experiments to determine the relative effects of dye concentration and dyeing pH on the quality of union shade, color strength, and dyebath exhaustion.

We have found that although the PDETAB fixative/union dyeing system is highly effective for union dyeing wool/cotton blended fabrics when wool reactive alpha-bromoacrylamido dyes are selected (union shades with high colorfastness properties), color strengths were relatively lower when compared to those of unpretreated wool dyed with these same dyes.

We have determined that PDETAB treated cotton has a limited number of dye sites, but if more cationic character could be conveyed to cotton, union dyeing system would be more efficient.

Previously, we described the wool component in the blends as "going along for the ride" in this system. However, microscopic observations showed that the wool fibers become coated by the fixative. This leads to dye retardation of wool and the possibility that the coating forms a pigment with the biguanide fixative that is released from the wool surface during dyeing or in the afterwash. This phenomenon could explain the poor colorfastness to wet crocking and home laundering, and further investigation is needed.

We have shown that in the case of an acid metallized dye, there is a limiting PDETAB concentration that can be recommended for achieving union shade. We have also shown that with this same dye, there is a limiting dye concentration that can be recommended for union shade. Overall, union dyeing systems that rely on fixative pretreatment as an expedient and direct route to union dyeing are potentially both effective and efficient, but, they must be based on experimentation to set optimum processing conditions.

Mention of brand or firm name does not constitute an endorsement by the U.S. Department of Agriculture above others of a similar nature not mentioned.

References

Blanchard, E. J. and R. M. Reinhardt. 1988. In Book of Papers, AATCC International Conference & Exhibition, Nashville, TN, 1988, 261 pp.

Blanchard, E. J. and R. M. Reinhardt. 1991. *American Dyestuff Reporter*, Vol. 80, No. 8, August, 73 pp.

Blanchard, E. J., et al. 1992. In Book of Papers, AATCC International Conference & Exhibition, Atlanta, GA, 1992, 270 pp.

Blanchard, E. J. and R. M. Reinhardt. 1992. *American Dyestuff Reporter*, Vol. 81, No. 11, November, 173 pp.

Cardamone, J. M., W. N. Marmer, F. F. Casado, G. Bao, G. Celikiz, J. Brady, J. Patel, J. Langan, M. Arifoglu, C. Sickerott, N. Hulton, J. McChesney III, G. Smith, R. Bamford, D. Fenstermaker, and F. Schuletsky. 1994. *Textile Chemist and Colorist*, Vol. 26, No.11, November, 29 pp.

Cardamone, J. M., W. N. Marmer, and E. J. Blanchard. 1995. In Proceedings of the 9th International Wool and Textile Research Conference, International Wool Secretariat, Biella, Italy, Vol. III, 71 pp.

Cardamone, J. M., G. Bao, W. N. Marmer, R. Dudley, and J. Bulan Brady. 1996. *Textile Chemist and Colorist*, Vol. 28, No. 12, 19 pp.

Cardamone, J. M., G. Bao, A. Francis, and W. N. Marmer. 1997. *Textile Chemist and Colorist*, Vol. 29, No. 9, 30 pp.

Cardamone, J. M., G. Bao, A. Francis, and W. N. Marmer. 1997. *American Dyestuff Reporter*, Vol. 86, No. 1, 41 pp.

Cardamone, J. M., W. N. Marmer, and J. G. Phillips. 1997. In Book of Papers, AATCC International Conference & Exhibition, Atlanta, GA, 388 pp.

Table 1. Color strengths of wool, cotton, and wool/cotton fabrics pretreated with PDETAB and union dyed with acid metallized dyes

Fabric Type	w/o PDETAB	Pretreated Alone	Pretreated Alone and Dyed Together
0.8g/100mL PDETAB/ 3% Lanasin Orange S-RL Powder (trivalent chromium complex of an azo dye)			
wool	29.2	25.4	26.8
cotton	2.0	14.0	12.8
62% wool/38% cotton			
		Pretreated	
	4.5	22.3	
4g/100mL PDETAB/ 3% Lanasin Orange S-RL Powder (trivalent chromium complex of an azo dye)			
wool	31.4	24.0	24.0
cotton	2.0	14.8	14.5
62% wool/38% cotton			
		Pretreated	
	5.5	22.5	
0.8g/100mL PDETAB/ 3% Intralan Navy SB (azo dye)			
wool	33.9	30.8	31.5
cotton	1.9	12.1	9.1
62% wool/38% cotton			
		Pretreated	
	4.3	19.2	
4g/100mL PDETAB, 3% Intralan Navy SB (azo dye)			
wool	29.8	23.0	21.3
cotton	2.2	13.0	11.4
62% wool/38% cotton			
		Pretreated	
	5.3	17.5	
0.8g/100mL PDETAB/ 3% Lanasin Black (trivalent chromium complex of an azo dye)			
wool	30.1	15.4	16.2
cotton	3.3	12.7	13.6
62% wool/38% cotton			
		Pretreated	
	5.4	18.7	
4g/100mL PDETAB/ 3% Lanasin Black (trivalent chromium complex of an azo dye)			
wool	30.1	15.4	16.2
cotton	3.3	12.7	13.6
62% wool/38% cotton			
		Pretreated	
	5.4	18.7	
4g/100mL PDETAB/ 3% Lanasin Grey S-BG (metallized azo dye)			
wool	31.5	18.2	16.9
cotton	3.7	13.6	14.3

% Dye vs. Color Strength

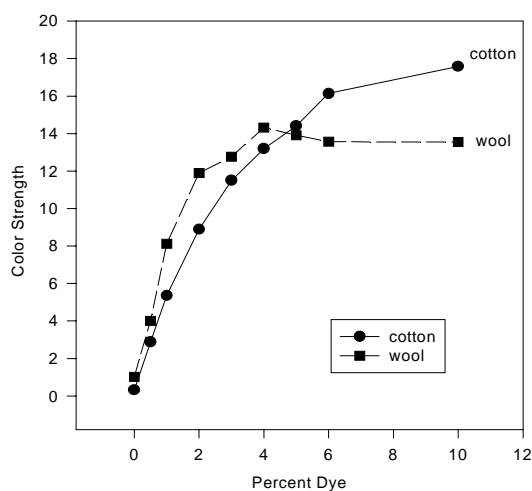


Figure 1. Effects of Lanasin Black S-GL Dye Concentration on the Color Strength of Cotton and Wool Fabrics Pretreated with 4g/100mL PDETAB

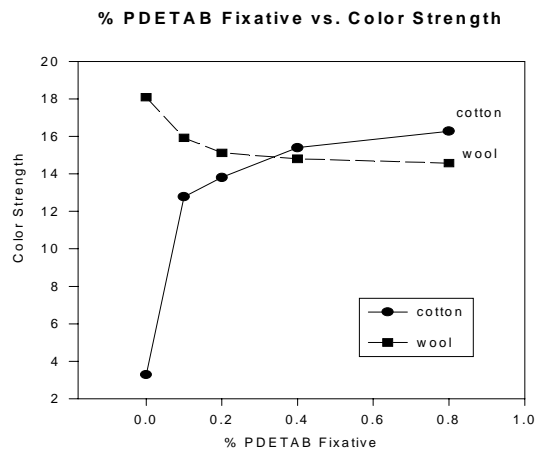


Figure 2. Effects of PDETAB Fixative Concentration on the Color Strength of Cotton and Wool Fabrics with 10% Lanasy Black S-GL