Union Dyeing Wool/Cotton Blends: Part I–Limiting Biguanide Concentrations For Union Dyeing With Wool Reactive Dye

Abstract

In ongoing ARS research on union dyeing wool/cotton blended textiles, commercial biguanide compounds were applied to 62% wool/38% cotton union cloth by exhaust and by padding to determine the lowest concentrations effective for subsequent union dyeing with wool reactive (alpha-bromoacrylamide) dye. A broad concentration range of 4% (4 grams/100 mL) on the weight of the bath (owb) to 4% (0.15 grams/100 mL) on the weight of the cotton (owc) constituent was evaluated for quality of union shade, color strength, and dyebath exhaustion.

Results showed that a 4% owc pretreatment bath was effective when applied by padding followed by dyeing with the wool reactive dye, C.I. Reactive Blue 69. When applied by exhaust, the lowest biguanide concentration effective for union shade was 6% owc. The potential to reuse the most concentrated baths, 4% owb and 2% owb, was also examined. Concentrations of 2% and 4% owb biguanide were effective for up to three to six reuses of the original pretreatment baths. Additionally, it was found that pretreatment baths of lowest concentrations (up to 6% owf) could be used as dyebaths in dyeing with C.I. Reactive Blue 69 when a biguanide-compatibilizing agent was added to the bath before the addition of the dye.

Introduction

The resurgent interest in wool/cotton blends is worldwide. These blends provide comfortable, resilient, and transseasonal attire for upscale leisure attire and professional women's wear. Processing problems such as efficiently dyeing wool and cotton to union shade have contributed to the limitations of yarn and fabric sources that are necessary to keep these blends in production. The ARS union dyeing process contributes to alleviating this complication. The process relies on applying biguanide compounds with guanidine and polyamino functions to selectively pretreat cotton in the presence of wool for subsequent one-step dyeing.[1,2,3,4,5] In this work, the limiting concentrations of biguanide are established for union dyeing these blends with wool-reactive dyes.

Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by USDA.

Experimental

Materials and Methods

Fabrics

Worsted wool yarns (68%, 2/24s) interlaced with pima cotton yarns (32%, 40s/2) of balanced plain weave, fabric count of 48x44 (TF4504), cotton fabric (TF400U print cloth), and wool fabric (TF523 worsted flannel, twill) were all obtained from Testfabrics, Inc., West Pittston, PA.

Fixatives/Pretreatment Baths/Procedures

A cationic biguanide dye fixative, Sandene 8425 Liquid (Clariant Corporation, Charlotte, NC), poly(diethylenetriaminebiguanide) sulfate, PDETAB, 55% solids, pH 6.5, designed for cationizing and aminizing cellulose for new dyeability was applied from baths constituted to 10:1 liquor ratio to pretreat 10 gram fabric samples at pH 6.5, 20° C for 60 minutes before union dyeing. The following biguanide concentrations were used: 4% owb (4 grams/100mL), 2% owb (2 grams/100 mL), 8% owf(0.8 grams/100mL), 6% owf (0.6g/100mL), 4% owf (0.4 grams/100 mL), 8% owc (0.8 grams x 0.32 = 0.25 grams/100 mL) and 6% owc (0.25 g/100mL), and 4% owc (0.19 g/100 mL) were constituted at liquor ratio (LR) 10:1.

The low bath concentrations were constituted from 2% (w/w) biguanide stock solutions. A pretreatment bath preparation involved adding the prescribed amount of water to bring the bath to volume. Pretreatment baths of elevated pH's were brought to volume with basic solutions of sodium hydroxide. The pretreatment process involved placing the fabrics in these baths and stirring occasionally throughout the time period. After pretreatment, the fabrics were rinsed thoroughly before adding them to fresh dyebaths.

Dyes/Dyeing

The wool reactive dye C.I. Reactive Blue 69 (Lanasol Blue 3G), Ciba Corporation, Greensboro, NC, with alpha-bromoacrylamide reactive groups was used to dye biguanide pretreated cotton (polyamino cationic cotton) in the presence of wool under nearly neutral conditions (pH 6.5, 3% dyeings). The bifunctional dye reacts selectively with cotton by nucleophilic substitution of bromine and by Michael Addition of cellulose to the double bond of the dye's reactive center. All dyeings were carried out pH 6.5 using the same time/temperature profile: 25 minutes at 20°C followed by a ramp rate of 1.5 degrees/minute to reach 95°C in 45 minutes for primary exhaustion, followed by secondary exhaustion at 95°C for 60 minutes. No salt was added. A leveling agent, Albegal B (1% owf), an amphoteric polyglycol derivative (Ciba Corporation), was added to the dye-

bath. The fabrics were aftertreated in a fresh bath with caustic at 70°C pH 8.5, for 10 minutes to remove surface and occluded dye.

Evaluation Methods

Effectiveness of pretreatment was determined in part by the color strength (K/S) of the dyed fabrics from a BYK-Gardner color measurement system that measures the reflectance of dyed fabrics. Image analysis was used to measure Union Shade Index, where the dyed fabric's digital image was expressed as a histogram representing pixel distribution over a brightness range of 256 gray levels. Nonunion shades exhibited bimodal histograms that could be resolved into two or three peaks. The mean values (X), areas (A), and standard deviations (S) of the individual resolving peaks were applied to an equation to measure Union Shade Index.[6]

Colorfastness testing utilized the standard AATCC Test Methods as follows: AATCC Test Method 61—Colorfastness to Laundering, Home and Commercial: Accelerated (Conditions IIA),AATCC Test Method 8—Colorfastness to Crocking, Crockmeter Method (wet and dry conditions), AATCC Test Method 132—Colorfastness to Drycleaning, and AATCC Test Method 16E—Colorfastness to Light (20 and 40 hours exposures, and AATCC Test Method 100—1993).

Padding and exhaust applications

Five 30 gram samples of the wool/cotton union fabric were pretreated by Clariant Corporation with Sandene 8425 Liquid by padding with approximately 100% wet pick-up on dry fabric at the following application levels as designated in Table I: 15.2g/L (4.0% owc), 22.8g/L (6.0% owc), 40.0g/L (4.0% owf), and 60.0g/L (6.0% owf). Padding conditions were pH 6.5, 20°C, by one dip and nip. In addition, a fabric was pretreated by exhaust under the conditions: Sandene 8425 Liquid (6.0% owf), 10:1 LR, pH 6.5, 60°C, 20 minutes. After rinsing the fabrics were dyed with 3% C.I. Reactive Blue 69 at pH 6.5. The dyed Clariant-pretreated fabrics (#1 to #5 in Table I) were compared to dyed ARS-pretreated fabric (#6) where biguanide was applied by exhaust with 4% owb Sandene 8425 Liquid at pH 6.5 for one hour at 20°C with LR 10:1.

Small color differences and approximately the same K/S and G-Values indicate that all applications were equally effective. Significantly less biguanide applied by padding at 4% owc can be used to attain the same union shade as biguanide applied at 6% owf to achieve the same result. Colorfastness properties are reported in Table II below, where numbers 1 to 6 correspond to the numbered samples in Table I.

Determining the Lowest Concentration of Biguanide to Apply by Exhaust for

Table I: Color Strengths, Color Differences, and Union Shade Indices of Wool/Cotton Union Cloth Dyed with 3% C.I. Reactive Blue 69 after Pretreatment.

	Pretreatment Conditions	Dyed Union Cloth		
		Delta E[a]	K/S[b]	G-Value[c]
1	exhaust, 6% owf	-	15.0	21.8
2	pad, 4% owc	0.65	14.3	21.9
3	pad, 6% owc	0.76	14.3	21.8
4	pad, 4% owf	0.32	15.5	20.0
5	pad, 6% owf	0.77	16.3	20.0
6	exhaust, 4% owb	0.75	15.0	20.6

* The dyedfabric from this pretreatment was adopted as the standardfor color difference, delta E.

[a] Overall color change includes CIELAB parameters for lightness, yellow-blue, and red-green. A delta E value of 1.00 units corresponds to just noticeable color difference.

[b] Color strength

[c] A G-Value threshold for Union Shade is 23.0 (n=1). This value corresponds to the visualperception of a nonunion-dyed textile for this sample set.

Table II: Colorfastness of Wool/Cotton Union Cloth Dyed with 3% C.I. Reactive Blue 69 after Pretreatment with Sandene 8425 Liquid Applied by Padding and Exhaust.

Sample	Crocking		Dry-cleaning	Laundering	Staining		Lightfastness	
	Dry	Wet			Cotton	Wool	20 hr	40 hr
1	4-5	2	5	4-5	4-5	4-5	5	4-5
2	4	1.5	5	4-5	4-5	4-5	4-5	4-5
3	4	1.5	5	4-5	4-5	4-5	4-5	4-5
4	4	2	5	4-5	4-5	4-5	5	4-5
5	4	1.5	5	4	4-5	4-5	5	4-5
6	4	1.5*	5	4-5	4	4-5	5	4-5

Value of 5 represent highest colorfastness.

*In past studies fastness to wet crocking received a rating of 3 and dry-crocking a value of 4-5 when Sandene 8425 Liquid was applied at 20% owb, for 3 hours, pH 11, at 20°C.[3]

Table III: Color Strengths and Union Shade Indices of Wool/Cotton Union Cloth Dyed with C.I. 3% Reactive Blue 69 after Pretreatment with Sandene 8425 Liquid Applied by Exhaust.

Sample	Concentration % Sandene 8425 Liquid	K/S	G-Value
1	4% owb	15.4	19.6
2	2% owb	15.4	20.2
3	1% owb	15.0	20.5
4	10% owf	14.6	21.7
5	8% owf	14.9	21.6
6	6% owf	14.4	21.0
7	4% owf	14.5	21.1
8	3% owf	14.0	21.5
9	6% owc	13.3	22.0
10	4% owc*	12.4	23.5*
11	3% owc*	12.4	24.2*
12	2% owc*	10.8	26.2*
13	1% owc*	7.4	35.2*

* A G-Value thresholdfor Union Shade is 23.0. This value corresponds to the visual perception of a nonunion-dyed textile for this sample set.

Union Dyeing Wool/Cotton Blends

The following concentrations of Sandene 8425 Liquid in Table III, were applied by exhaust at conditions of pH 6.5, one hour, 20°C, LR 10:1 to determine the limit of biguanide concentration effective for union shade when dyed with 3 % owf C.I. Reactive Blue 69.

The colorfastness properties of these dyed fabrics pretreated within the biguanide within the concentration range of 4% owb to 6% owc are found in Table III, where numbers 1 to 9 correspond to numbered samples in Table III.

The 4% owb and 2% owb Sandene 8425 Liquid pretreatment baths in Table m were used successively as pretreatment baths for union dyeing with 3% C.I. Reactive Blue 69. Effectiveness was determined from the K/S and G-Values shown in Table V.

Note that the difference in color strength, K/S, from the 1st to the 6th bath for 4 % owb is 3.7 units and for 2 % owb is 3.6 units. These are visually perceptible color differences. Colorfastness properties of the dyed fabrics from Table V are shown in Table VI.

Determining the Use of Biguanide Pretreatment Baths as Dye Baths for Union Dyeing wool/cotton Blends

Used pretreatment baths remain cationic because of the presence of residual biguanide. This presents a complication if they are to be used subsequently as dyebaths. To overcome incompatibility with anionic dye, a compatabilizing agent, Mesitol NBS Liquid (Bayer Corporation, Rock Hill, SC), the condensation product from aryloxysulfonic acid, was added to a 4% owb pretreatment bath after its first use. Then 3% C.I. Reactive Blue 69 was added. Preteatment baths of concentrations: 4% owf (0.4g/100mL), 3% owf (0.3g/100mL), 2% owf (0.2g/100mL), and 1% owf (0.1g/100mL) were made compatible by adding 2 drops Mesitol reagent. The dyed fabrics from these dyebaths exhibited the respective K/S values of 9.2, 8.6, 8.6,8.3. Note that these values were significantly lower than those for 4% owf, 3% owf, and 6% owc in Table III, where fresh dyebaths were used. Thus, even though it was feasible to reuse a biguanide bath as a dyebath for low concentration it proved impractical because the dyed fabrics exhibited significant loss in color strength.

Conclusions

The strong affinity of biguanide compounds for cotton cellulose can be used

Table IV: Colorfastness of Wool/Cotton Union Cloth Dyed with 3% C.I. Reactive Blue 69 after Pretreatment with Sandene 8425 Liquid Applied by Exhaust.

Sample	Crocking		Dry-cleaning	Laundering	Staining		Lightfastness	
	Dry	Wet			Cotton	Wool	20 hr	40 hr
1	4-5	2	5	4	4	4-5	4-5	4
2	4	2	5	4	4	4	4-5	3-4
3	4-5	2	5	4	4	4-5	4	3-4
4	4-5	2	5	4	4-5	4-5	4	4
5	4-5	2	5	3-4	4	4-5	4-5	3-4
6	4-5	2	5	3-4	4-5	4	4-5	4
7	4-5	2	5	5	3-4	4-5	4-5	4
8	4-5	2	5	4	4-5	4-5	4-5	4
9	4-5	2	5	3-4	3-4	4-5	4	3-4

Table V: Color Strengths and Union Shade Indices of Wool/Cotton Union Cloth Dyed with C.I. 3% Reactive Blue 69 after Successive Pretreatment with 4% owb and 2% owb Sandene 8425 Liquid Applied by Exhaust.

Pretreatment	K/S		G-Value	
% Sandene 8425	4% owb	2% owb	4% owb	2% owb
original bath	16.2	15.4	20.3	20.0
2nd reuse	14.0	15.0	21.5	20.5
3rd reuse	14.6	14.2	20.6	20.7
4th reuse	13.1	12.1	22.2	22.3
5th reuse	12.7	11.9	22.0	22.7
6th reuse	12.5	11.8	22.5	22.6
7th reuse	11.7	11.3	23.0	23.9
8th reuse	11.4	10.1	23.7	24.6
9th reuse	10.9	8.6	23.1	27.8

* A G-Value thresholdfor Union Shade is 23.0. This value corresponds fo the visual perception of a nonunion-dyed textile for this sample set.

Table VI: Colorfastness of Wool/Cotton Union Cloth Dyed with 3% C.I. Reactive Blue 69 after Successive Reuses of the Bath Containing Original Concentrations of 4% owb and 2% owb Sandene 8425 Liquid Applied by Exhaust.

%Sandene 8425	Crocking		Dry-cleaning	Laundering	Staining		Lightfastness	
	Dry	Wet			Cotton	Wool	20 hr	40 hr
4 % owb								
original bath	4-5	2	5	5	4-5	4-5	4-5	4
2nd reuse	4 5	2	5	5	3-4	4-5	4-5	4
3rd reuse	4	2	5	4	4	4	4-5	4
4th reuse	4-5	2	5	4	4	4-5	4-5	4
5th reuse	4-5	2	5	3-4	4	4	4-5	4
6th reuse	4-5	2	5	3	4	4	4-5	4
2 % owb								
original bath	4	2	5	3-4	4-5	4-5	4-5	4
2nd reuse	4	1-2	5	3-4	4-5	4-5	4-5	4
3rd reuse	4-5	2	5	3	4	4-5	4-5	4
4th reuse	4-5	2	5	3	4	4-5	4-5	4
5th reuse	4-5	2	5	3-4	3-4	4-5	4-5	4
6th reuse	4-5	2	5	3-4	3-4	4-5	5	4-5

*In past studies fastness to wet crocking received a rating of 3 and dry-crocking a value of 4-5 when Sandene 8425 Liquid was applied at 20% owb for 3 hours pH 11, at 20°C.

to improve the union dyeing of wool/cotton blended textiles. Biguanide-modified cotton contains cationic charge and polyamino functionality for union dyeing with acid or reactive dyes under nearly neutral conditions without salt. Pretreatment variables that can influence union dyeing include biguanide concentration, pH, time, and temperature, and dyeing variables include dye selection, concentration, dyebath pH, and dyeing procedure.

Application of biguanide by padding and subsequent dyeing with 3% C.I. Reactive Blue 69 produced union shades that required only 1/4th the amount of the exhaust application. The colorfastness properties of the union dyed fabrics from both application methods were essentially identical and excellent except for colorfastness to wet crocking, which imposed a recommendation for outerwear enduse and dry-clean only. The lowest effective biguanide concentration by padding for dyeing to union shade with high color strength was found to be a small amount, 6% owc. The colorfastness properties of these fabrics from 6% owc pretreatments were no different from those of the union dyed fabrics pretreated with the much higher concentration of 4% owb.

For pretreatment applications by exhaust with biguanide concentrations from 4% owb to 1% owc, 6% owc was found to be the limiting concentration for union shade when dyeing with 3% C.I. Reactive Blue 69. Union dyed blends that had been pretreated with 6% owf biguanide, however, exhibited higher color strengths.

The efficiency of the Sandene 8425 Liquid pretreatment bath was demonstrated by finding that the original 2% owb and 4% owb baths could be reused up to six times provided that a slight loss in color strength can be tolerated. The colorfastness properties of the union dyed fabrics from these reused baths were essentially the same as those that had been processed from the original pretreatment baths.

Overall, pretreatment with this biguanide compound provides an expedient method for union dyeing by padding and exhaust and these methods are efficient and economically sound. From this work, the lowest pretreatment conditions of biguanide concentration (8% owf), pH (6.5), time (15 minutes), and temperature (20°C) can be recommended as having no adverse affect on color strength, dyebath exhaustion, and the qualities of level and union shades when dyeing with the wool reactive dye examined in this study. □ □ □

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