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MARY ANN MORRIS
and
BARBARA W. MITCHELL

UNIVERSITY OF CALIFORNIA · BERKELEY, CALIFORNIA

The whitening effect of a fluorescent dye applied from organic solvents to white wool was investigated. Optimum conditions for applying C. I. Fluorescent Brightening Agent #68 from perchlorethylene and Stoddard solvent at room temperature were developed. Visual evaluation in daylight and under ultraviolet light showed a marked improvement in whiteness after application of the dye to white wool fabrics. The fastness of the dye to conditions encountered during use was found to be satisfactory.

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MARY ANN MORRIS[2] and BARBARA W. MITCHELL[3]

INTRODUCTION

WHITE WOOL FABRICS and garments may turn yellow with use or age. Materials commonly used to improve whiteness, such as aqueous solutions of oxidizing or reducing bleaching agents, may damage wool fibers and also cause shrinkage. A method for improving whiteness without such damage would therefore be of value.

The application of fluorescent dyes from organic solvents is a possible technique for improving the whiteness of garments that have become yellowed. Such dyes have been widely used in the detergent, paper, and textile industries—in the latter mainly to improve the whiteness of cellulosic materials. However, a dye giving good results on cellulosic materials could not be expected to give the best results on wool, because of differences in the chemical nature of the two fibers. In addition, these cellulosic dyes, which are highly soluble in water, may have very limited solubility in organic solvents.

Fluorescent dyes are compounds that absorb invisible ultraviolet radiation and emit visible light when applied to textile fabrics. This fluorescence provides the light required to compensate for unfavorable fabric yellowness. These substances may be classified as dyes, since they affix themselves to a fabric and influence fabric color.

A fluorescent dye should have a good affinity for the fiber to which it is applied, should be adequately soluble for satisfactory application, produce a desirable shade, and be relatively stable to the conditions encountered during use. The dyes selected for a particular fiber, to be satisfactory, should give a fluorescence which produces a desirable white tint when combined with the natural hue of the fiber. Since dyes fluoresce in different colors, the effect of a particular dye combined with colors of different substrates will not always give the acceptable tint of white (Weber, 1958).[4] Furthermore, the tint of white considered acceptable varies with fiber content. Casper (1950) states that while bluish, chalky whites are acceptable for cotton fabrics, a milky, greenish tint is more desirable for wool materials. This

[1] Received for publication March 22, 1960.

[2] Associate Professor, Department of Nutrition and Home Economics, Berkeley.

[3] Assistant Home Economist, California Agricultural Experiment Station, Berkeley.

[4] See "Literature Cited" for citations referred to in the text by author and date.

being the case, dyes developed for cellulose fibers may not give a satisfactory tint when applied to wool.

The use and development of fluorescent dyes as brightening agents have been somewhat hampered by lack of a standard method of evaluating their effectiveness. Laboratory instruments have been modified and new ones developed for this purpose (Allen, 1957; Furry and Bensing, 1955; Glarum and Penner, 1954; Sherburne and Beiswanger, 1952; Taylor, 1955) but no specific one appears to be generally accepted. Visual examination in daylight and under ultraviolet light has been widely used. Allen (1957) states that visual evaluation in daylight is the most accurate method since it gives the best over-all estimate of whiteness. However, this method lacks precision, since slight differences are not easy to detect and the spectral quality of daylight varies. Allen (1957) also considers visual evaluation under ultraviolet light to be an excellent method for evaluating brightening agents if the same fluorescent dye is used for all dyeings.

The evaluation of a fluorescent dye in its effectiveness in improving the whiteness of wool, when applied from selected organic solvents, has been studied.

PROCEDURE

Development of Optimum Dyeing Conditions.—C. I. Fluorescent Brightening agents #45, #57, #68, #69, #70, and #72 (Soc. Dyers and Colourists, Amer. Assn. Textile Chemists and Colorists, 1956) reported to be soluble in organic solvents, were obtained for evaluation from major dye producers in the United States.

The organic solvents, perchlorethylene and Stoddard solvent, were used throughout the experiments. Dyeing was done at room temperature because of the volatility and flammability of the solvents. The dye was applied to 5-inch square swatches of the control fabric, an unbleached, scoured, worsted and woolen flannel (table 1).

The amounts of dye, wetting agent, and water added to the dye bath were varied. The volume of solvent (132 ml), fabric weight, agitation rate, time, and solvent temperature were held constant. Cationic, anionic, and nonionic wetting agents were investigated. The components of the dye bath were placed in a pint jar, the fabric swatch was added, and the jars were agitated at 42 rpm for 30 minutes in the Launderometer. The unextracted samples were hung to air-dry. Wrinkles were removed from the dry samples by hand-pressing with a steam iron.

Effect of the dye bath variables on the control fabric was visually evaluated in both daylight and under an ultraviolet lamp. Daylight evaluation was made in a room where there was no reflectance from neighboring buildings. Samples were viewed in light from the northern sky, coming through large, high windows located directly above the sample viewing area, a flat surface covered with white cardboard (91-lb Bristol Index). All evaluations were carried out on overcast days, between 8 and 10 a.m., in order to keep variation in the spectral quality of the light at a minimum. Ultraviolet evaluations were made in a darkroom, under a lamp equipped with a spot-type, 100-watt, long-wave, ultraviolet bulb which produced concentrated 3660Å rays. The lamp had a red-purple filter, specially selected to transmit long-wave ultraviolet rays. The samples were placed in a position where rays from the lamp struck them at a 45-degree angle. All visual evaluations were made by the same two observers.

Color differences were also measured on a Gardner Automatic Color Difference Meter, using the R_d color difference scale. The three values of the scale are R_d, a, and b. R_d is a measure of light reflectance. Plus values for a indicate redness; minus values indicate greenness. Plus values for b indicate yellowness; minus values indicate blueness. Color differences also were calculated in NBS units (Nickerson, 1944). Four thicknesses of fabric backed by a suitable standard were used during color readings.

TABLE 1

FABRICS USED IN THE DEVELOPMENT AND EVALUATION OF FLUORESCENT DYEING PROCEDURES

Fabric	Initial color measurement*			Fabric weight
	R_d	a	b	oz/sq yd
Control wool fabric				
Unbleached worsted and woolen flannel	61.5	+0.6	+11.7	7.3
Yellowed wool fabrics from worn garments				
White worsted gabardine	55.8	+2.0	+15.2	8.8
White woolen fleece	56.6	+2.4	+17.0	10.7
Colored wool fabrics				
Red worsted jersey	10.7	+65.2	+20.2	4.9
Yellow worsted jersey	39.0	+7.1	+35.0	4.9
Blue worsted jersey	9.2	+0.3	−27.8	4.9
Fabrics of varying fiber content				
White cotton percale	86.8	+0.6	+1.8	3.5
White rayon filament twill	100.3	0.0	+6.7	3.8
White acetate filament taffeta	82.2	−1.1	+4.2	2.7
White silk shantung	81.2	−0.1	+4.2	2.2
White nylon filament taffeta	83.1	−0.4	+1.6	2.5
White Dacron filament pique	79.0	−0.4	−1.8	2.7
White Orlon filament taffeta	82.1	−0.2	+7.8	2.1

* Measured with Gardner Automatic Color Difference Meter.

Evaluation of Dyed Fabrics.—After the optimum dyeing conditions were developed, the over-all permanence of the fluorescent dye on the worsted and woolen flannel was evaluated. The visual evaluation techniques have been described above.

Standard AATCC procedures (Amer. Assn. Textile Chemists and Colorists, 1958) were used for measuring colorfastness to crocking (8-1957), perspiration (15-1957), and light (16A-1957). The effect of steam pressing was determined with a home-type steam iron. After pressing and before evaluation, samples were allowed to equilibrate at room temperature. The permanence of the fluorescent dye to Stoddard solvent and perchlorethylene was determined by agitating dyed fabrics in the respective solvents for 30 minutes in the Launderometer.

To evaluate further the efficiency of the fluorescent dye and the application technique, three groups of fabrics were dyed under conditions developed for the control fabric, namely, white wool fabrics yellowed with age, colored wool jersey, and white fabrics of various natural and chemically manufactured fibers (table 1). Dyed samples of each of the fabrics listed in table 1 were aged in total darkness for 24 weeks, under constant temperature and humidity conditions (70°C, 65 per cent RH). The fabrics were evaluated for color changes visually in daylight, and with the Gardner Automatic Color Difference Meter at two-week intervals for three months, and thereafter at four-week intervals.

DISCUSSION

Optimum Dyeing Conditions

The degree of solubility in perchlorethylene and Stoddard solvent was determined for the fluorescent dyes studied. These solvents were chosen because they are commonly used for drycleaning. A dye classified as C. I. Fluorescent Brightening Agent #68 was found to have the greatest degree of solubility in perchlorethylene and Stoddard solvent, and was therefore used for all further experimentation.

Preliminary work indicated that agitation for approximately 30 minutes was adequate for maximum dye pickup.

Improvement in whiteness of the control fabric was negligible when a fluorescent dye was used alone, regardless of dye concentration. Addition of wetting agents to the solvent resulted in a slight increase in fabric whiteness, and addition of both water and wetting agent resulted in an even greater improvement. A nonionic wetting agent, polyoxyethylene alkyl aryl ether, was found to be the most effective, of those investigated, in increasing dye pickup. No improvement was noted when water alone was added to the solvent.

TABLE 2

OPTIMUM DYEING CONDITIONS DEVELOPED FOR UNBLEACHED CONTROL WOOL FABRIC

Dye bath components	Solvent	
	Stoddard	Perchlorethylene
C. I. Fluorescent Brightening Agent #68	0.75%*	1.9%*
Nonionic ether wetting agent	57.8%*	67.5%*
Water	24.0%*	13.5%*
Liquor ratio	1:26	1:54

* Per cent on weight of fabric.

On the basis of these preliminary findings, the optimum proportions of dye, wetting agent, and water for improving the whiteness of the control fabric were studied. Optimum application conditions for each of these variables in the two solvents, as measured by visual and ultraviolet evaluation, are shown in table 2. Variation of the reagents above the percentages shown in the table resulted in no additional improvement in whiteness, while a decrease in percentages reduced the apparent whiteness.

Evaluation of Dyed Fabrics

White Wool Fabrics.—Application of the fluorescent dye under the conditions described in table 2 resulted in a significant improvement of the whiteness of the control fabric as determined by visual evaluations (table 3). This improvement in whiteness, or decrease in yellowness, was also found in determinations on the Color Difference Meter. The values for the *b* readings showed a decrease in yellowness of the control fabric. Color differences, according to NBS units, also indicated a change between the color of the undyed control and the dyed control.

TABLE 3

COLOR DIFFERENCES BETWEEN UNDYED ORIGINAL FABRICS AND FLUORESCENT DYED FABRICS

Fabric	Solvent					
	Perchlorethylene			Stoddard		
	Visual daylight evaluation	Color difference meter measurements		Visual daylight evaluation	Color difference meter measurements	
		b*	NBS units		b*	NBS units
A. Initial differences						
Woolen and worsted flannel (control)	whiter	−3.0	3.5	whiter	−3.0	3.4
Yellowed worsted	whiter	−2.6	3.7	whiter	−2.0	2.8
Yellowed woolen	whiter	−2.4	2.5	whiter	−2.4	2.6
Cotton	whiter	−0.9	3.6	whiter	−3.2	4.8
Rayon	whiter	−1.1	3.2	whiter	−2.3	5.7
Acetate	whiter	−3.2	5.1	whiter	−4.6	6.2
Silk	whiter	+1.5	7.4	whiter	−3.0	5.5
Nylon	whiter	−4.6	5.6	whiter	−4.4	6.5
Dacron	whiter	−0.5	1.2	whiter	−2.6	3.1
Orlon	whiter	−2.0	2.4	whiter	−2.2	3.6
B. Differences after ageing 24 weeks						
Woolen and worsted flannel (control)	whiter	−2.6	3.2	whiter	−2.8	3.2
Yellowed worsted	whiter	−2.4	3.0	whiter	−1.8	2.8
Yellowed woolen	whiter	−2.2	2.6	whiter	−2.6	2.7
Cotton	slightly green	+2.3	5.0	whiter	−1.7	4.9
Rayon	greyed	+0.4	4.7	whiter	−1.8	6.6
Acetate	whiter	−1.3	3.7	whiter	−1.2	4.0
Silk	greyed	+1.4	7.0	slightly greyed	−2.2	5.5
Nylon	whiter	−0.8	2.8	whiter	−1.8	2.5
Dacron	greyed	+2.2	4.2	whiter	−2.0	2.8
Orlon	whiter	−0.5	2.7	whiter	−1.8	2 6

* Toward blue in minus direction; toward yellow in plus direction.

Whiteness of the white wool gabardine and fleece fabrics was also improved by application of the dye according to the proportions in table 2. These fabrics were obtained from worn garments that had become decidedly yellowed. As indicated in table 3, both visual and Color Difference Meter evaluations showed a decrease in yellowness for the treated fabrics.

This improvement in whiteness was quite permanent to ageing for all white wools. After storage in total darkness for 24 weeks, the fabrics showed only a negligible change in *b* values and a slight change in NBS units. These slight changes could not be detected visually (table 3).

Frequently, fluorescent dyes have been found to have poor lightfastness. Adams (1958) found that fastness to light of fluorescent dyes used on wool is somewhat inferior to that of such dyes used on cellulosic materials. The original improvement in whiteness produced by the dye may be quickly eliminated by the decomposition products of dyes that have poor lightfastness. The dyed material may even look darker than the undyed control fabric if the decomposition products are colored (Casper, 1950). Therefore, the fastness to light of the C. I. Fluorescent Brightening Agent #68 was determined for the control fabric, the aged gabardine fabric, and the aged fleece. After 20 hours' exposure in the Fadeometer, all three fabrics had yellowed considerably. The exposed area of the dyed control fabric was not so yellow as the undyed control fabric when evaluated visually in daylight. However, the exposed areas of the dyed gabardine and fleece were judged to be of the same degree of yellowness as the undyed fabrics. In no case were the exposed dyed fabrics judged to be darker than the undyed materials. These results substantiate Adams' recent statement (Adams, 1958) that most present-day fluorescent brightening agents have at least moderate lightfastness and are free from any tendency to discolor. Graham and Stratham (1956) report that the presence of fluorescent agents on wool did not cause any greater ultimate discoloration in light than was found on undyed exposed wool.

Colorfastness of the fluorescent dye to crocking, perspiration, steam pressing, and solvent was determined. All of these factors can cause color change, and little has been reported on the effect of these agents on the colorfastness of fluorescent-dyed materials. None was found to affect the color of the dyed control fabric when evaluated visually in daylight. Also, no color changes were found by visual evaluation under ultraviolet light except in one case. A slight loss of fluorescence was noted on the dyed control fabric after treatment with perchlorethylene and Stoddard solvent. Also noted was a slight transfer of dye to the cotton test cloth in the crocking test, although there was no change in the appearance of the control.

Colored Wool Fabrics.—While fluorescent dyes are used to improve the whiteness of fabrics, it is desirable that these agents have no adverse effect on other colors. The color of trim or linings that are permanently attached to a white garment should not be dulled by the application of a fluorescent dye.

The C. I. Fluorescent Brightening Agent #68, when applied to red, blue, and yellow worsted jerseys (table 1) produced a decrease in R_d values (table 4). The initial decrease in reflectance was greater for the yellow fabric than for the red and blue materials. No change in color was observed by visual examination in daylight; nor was there a detectable dulling of colors as a result of the brightening agent. Adams (1958) has stated that the effect of brighteners on deep colors is negligible, but that quite marked effects could be produced on pastel shades. A somewhat similar effect was found on the colored jerseys, since there was initially a greater change on the lighter, yellow fabric than on the two darker colors. After the fabrics were aged in total darkness for 24 weeks, no change in color was observable by visual daylight examination. Very slight variations in reflectance readings and NBS units were obtained on the aged fabrics (table 4).

Fabrics of Varying Fiber Content.—Fluorescent dyes which improve the whiteness of wool cannot be expected to give good results on all other fibers. However, dyes to be used on garments should not cause a discoloration on fabrics of any fiber content.

The degree and shade of the brightening effect produced by fluorescent dyes depend on the character of the substrate, the surface of the fabric (dull, lustrous, smooth, rough), the thickness of the fabric or of the yarn, and the type of weave (Siegrist, 1955). Because of the influence these factors might

TABLE 4

COLOR DIFFERENCES BETWEEN THE ORIGINAL COLORED FABRICS AND THE FLUORESCENT DYED COLORED FABRICS

Fabric	Solvent					
	Perchlorethylene			Stoddard		
	Visual daylight evaluation	Color difference meter measurements		Visual daylight evaluation	Color difference meter measurements	
		R_d*	NBS units		R_d*	NBS units
A. Initial differences						
Blue wool	no change	−0.8	1.5	no change	−1.2	2.6
Red wool	no change	−0.2	0.9	no change	−0.8	3.0
Yellow wool	no change	−3.4	3.1	no change	−4.7	4.3
B. Differences after ageing 24 weeks						
Blue wool	no change	−0.6	1.1	no change	−0.9	1.6
Red wool	no change	−0.8	0.6	no change	0.0	4.1
Yellow wool	no change	−2.9	2.7	no change	−4.7	4.3

* Decrease in reflection in minus direction; increase in reflection in plus direction.

have, white fabrics of varying fiber content and surface character were dyed under the optimum dyeing conditions (table 2). The fabrics used in this phase of the study are listed in table 1. After treatment with the dye, the white fabrics were in every case judged visually in daylight to be whiter than the original fabric (table 3). It may also be noted that the *b* values and the NBS units of color difference indicate a color change from the original. After ageing in total darkness for 24 weeks, some fabrics (rayon, acetate, Orlon, Dacron, silk, and cotton) showed signs of discoloration (table 3). However, this discoloration was not severe in any case.

The reliability of the visual evaluations in daylight and under ultraviolet illumination was greatly increased because all dyeings were made using C. I. Fluorescent Brightening Agent #68 (Allen, 1957). The *b* values obtained on the Color Difference Meter agreed in general with the color changes noted visually. In almost all cases, decreases in *b* values were associated with a visual evaluation indicating an improvement in whiteness.

SUMMARY

The improvement in whiteness of white wool fabrics resulting from the application of C. I. Fluorescent Brightening Agent #68 was studied. The dye was applied, on a laboratory scale, from perchlorethylene and Stoddard solvent. The dyed fabrics were evaluated by visual examination in daylight and under ultraviolet light, and with a Gardner Automatic Color Difference Meter.

The greatest improvement in the whiteness of the wool fabric was obtained when water and a wetting agent were incorporated in the dye bath under the conditions of this investigation. For these laboratory-scale dyeings, the proportions of dye, wetting agent, and water that gave optimum results on the wool control fabric were determined.

On the unbleached control fabric, application of the fluorescent dye by the optimum dyeing conditions resulted in a marked improvement in whiteness. An improvement was also observed when two wool fabrics that had become yellowed during use were dyed by the same method.

This initial improvement in whiteness on the three wool fabrics was found to be unchanged after ageing for 24 weeks in total darkness.

Exposure of the three wool fabrics in the Fadeometer for 20 hours caused yellowing of all fabrics. However, in no case were the exposed, dyed fabrics judged to be darker than the undyed materials.

The dye on the unbleached control fabric was found to be fast to crocking, perspiration, steam pressing, Stoddard solvent, and perchlorethylene.

The application of the fluorescent dye to blue, red, and yellow worsted jerseys did not produce color changes observable by visual examination in daylight. In addition, no change in the color of these fabrics was found after 24 weeks of ageing in total darkness.

White cotton, acetate, rayon, silk, nylon, Dacron, and Orlon fabrics were judged visually in daylight to be whiter than the original fabrics, after being dyed with the fluorescent dye under the optimum conditions of this study. Slight changes in color were observed on some of the above fabrics after ageing in total darkness for 24 weeks.

The results indicate that the treatment of wool with fluorescent dyes in organic solvents offers possibilities as an effective method for improving whiteness. While this exploratory study has been on a laboratory scale, the findings show promise for adaptation to large-scale applications.

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