Big John or Pitch

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Surface Modification

Enzymatic Treatment of Man-made Cellulosic Fabrics

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ABSTRACT

Cellulases have been used in garment wet processing for approximately eight years. The majority of cellulase enzyme used in textile applications has been on cotton. Denim jeans and knit and woven cotton garments are frequently treated. Cellulases effectively improve cotton's surface appearance, handle and drape, and reduce its tendency to pill or fuzz after repetitive launderings.[1-4] Today, cellulases are also being used to benefit man-made cellulosics.

In this study, several man-made cellulosic fabrics—lyocell (Tencel), rayon (viscose) and cellulose acetate—were treated with cellulase. The treated fabrics and untreated controls were tested for surface fuzz removal, softening, pilling, weight and strength.

The effect of cellulase on these different cellulosics varied. On both rayon and lyocell, cellulase altered the handle and drapeability and removed surface fuzz. Cellulase also reduced the tendency of rayon to pill and reduced fibrillation of lyocell. Cellulose acetate was minimally affected by cellulase under the selected test conditions.

KEY TERMS

Cellulase
Cellulose Acetate
Enzyme
Lyocell
Rayon
Tencel
Viscose

Lyocell is the generic name for solvent spun cellulosic fibers which Courtaulds plc has branded as Tencel. Courtaulds is presently the only commercial producer of lyocell fibers. Lyocell is a new fiber spun from wood pulp in a closed amine oxide solvent system.[5] The solution is then filtered and extruded to form the filaments. The resulting dissolved cellulose fiber has similar amounts of amorphous and crystalline cellulose and degree of polymerization of the wood pulp starting material.[6] The fiber cross section is highly regular and cylindrical. Tangles of primary fibrils are visible on the surface prior to cellulase treatment. Attributes of lyocell include luxurious drape, diverse range of tactile properties, ease of blending with other fibers, high wet modulus, good wash stability resulting in low shrinkage and environmental "friendliness."[7]

Rayon (viscose) is a regenerated cellulosic fiber. The process involves dissolving wood pulp in an inorganic solvent containing sulfur and extruding the fiber. The fiber cross sections are highly irregular and crenelated. As with lyocell, loose surface fibers are evident prior to cellulase treatment. The Textile Fiber Products Identification Act (TFPIA) defines rayon as "a manufactured fiber composed of regenerated cellulose, as well as manufactured fibers composed of regenerated cellulose in which substituents have replaced not more than 15% of the hydrogens of the hydroxy radicals." Rayon has about 30-fold lower degree of polymerization than cotton and 40% degree of crystallinity versus 60% for cotton.[8] The crystalline structure of rayon (and regenerated cellulose in general) consists of primarily type II cellulose-oriented (anti-parallel) polymers; as opposed to type I (parallel) crystallinity in natural cellulosics.[8] Rayon defines a fairly broad category of fibers with a similar range of physical properties. Some general characteristics of rayon include a relatively low resiliency (particularly when wet), high absorption and soft hand.[9] Since rayon can be processed into either filament or staple form, rayon offers more variety in fabric and yarn construction than do natural cellulosic fibers. Rayon fibers are widely used in apparel, home furnishings and industrial materials.

Cellulose acetate is a chemically modified cellulosic material. The process uses cellulose from wood pulp or cotton linters which is acetylated and eventually extruded to form the spinning fibers. Acetate is defined by the TFPIA as "a manufactured fiber in which the fiber-forming substance is cellulase acetate. Where not less than 92% of the hydroxyl groups are acetylated, the term triacetate may be used as a generic description of the fiber." The degree of polymerization and type of crystalline cellulose is similar to that of rayon, however the acetate fiber has proportionately more crystalline structure.[9] Acetate's strong dimensional stability has been used for blends in a variety of woven and knitted fabrics.

Despite the specificity of cellulases for ß 1-4 glucosidic bonds, both regenerated and chemically modified cellulose are susceptible to cellulytic hydrolysis. However, the activity of cellulase for a given substrate is dependent on a number of factors such as the amounts of non-cellulosic wood pulp-derived matter, the degree of polymerization, the type and degree of crystallinity, and the type and number of chemical substitutions to the cellulose.[8,10,11] Cellulases require an amorphous polymer surface and access to the ß 1-4 glucosidic bonds. Highly crystalline (particularly type II) or chemically substituted cellulose are thought to be less susceptible to hydrolysis by cellulase.

Though cellulases alone can effectively hydrolyze cellulosic materials, commercial wet processing piece goods or garments with enzymes must also include some hydromechanical force. The role of the mechanical action is crucial because it accelerates surface fiber removal allowing for acceptable amounts of weight loss and strength loss. The degree of mechanical action is dependent on what type of equipment is used.

Finally, it should be noted that enzymes are complex molecules with several functional activities. The number and type of components represented within commercially available cellulases vary considerably, and subsequently produce different effects.[12] For simplicity, in this study a fungal acid cellulase was used which has optimum activity at a pH of 5.

Methods

Lyocell (Tencel), rayon (viscose) and cellulose acetate woven fabrics of medium and heavy weight were treated with an acid cellulase for up to 120 minutes in a 35 kg-lab scale rotary drum washer. The resulting fabrics were tested for differences in surface smoothness, handle, weight, strength and laundering durability. See Table I for the method used to test each of the attributes. The results along with potential benefits are described later.

The dose used in this study is higher than recommended on commercial scale equipment. This is because the mechanical action produced on fabric in this lab scale equipment is significantly lower than that achieved with commercial equipment.

Results And Discussion

The effects of treating man-made cellulosic fabrics with cellulases were measured on a pilot scale and correlated well to results in commercial applications.

Fig. 1 shows the surface modification following a 3 g/L , 60-minute cellulase treatment of the man-made lyocell fabric. A similar reduction of loose surface fibers is seen on rayon as well as on natural cellulosic fibers. Cellulase treatment modifies the fabric handle, drape and surface appearance.

Table I. Attribute and Method of Testing Used to Evaluate Samples

Attribute	Method of Testing
Handle	Force of Compression Energy
Tensile Strength	Breaking Force and Elongation of Textile Fabrics; (Grab Test) ASTM D 5034
Fuzz Removal	Scanning Electron Micrographs and Panel Score
Pilling	Random Tumble Pilling Tester Method ASTM D 3512-76

Figs. 2 and 3 show the effect of cellulase treatment of lyocell on a more microscopic scale. An important distinction of lyocell is that the cellulase is cleaving primary fibrils rather than entire loose fibers as in rayon and natural cellulosics. This occurs because of the differences in wet fiber tenacities. Ordinarily, the cellulase hydrolyzes a portion of the fiber, and with the hydromechanical action, the weakened fiber is sheared off. But lyocell has such high wet strength that only an outer shell tends to be cleaved.

Fig. 4 shows that in addition to surface fuzz removal, the tendency for pilling to occur—in fabrics that are prone to pilling—is reduced. The rayon twill weave fabric treated with cellulase showed a significant reduction in the tendency to pill which became more pronounced following multiple home launderings. The pilling reduction effect also occurred within the first 60 minutes of processing with cellulase.

Within the selection of fabrics for this study, only the rayon twill was prone to marked pilling. Despite the presence of noticeable surface fuzz on a number of the samples, pills did not form because of the particular fiber tenacities. Some benefits have been observed by treated cellulosic-synthetic fabric blends. However, a reduction in pilling was noted only when the pills were comprised of cellulosic and not synthetic material. Again, in these synthetic-cellulosic blends such as rayon-lycra, cellulase treatment does not effect the synthetic material, but did smooth the surface of rayon and eliminate rayon pills.

The reduction in compression energy shown in Fig. 5 suggests a softening in the fabric handle. The lyocell and rayon samples exhibited reduced compression energy. Cellulose acetate data indicated no significant change in

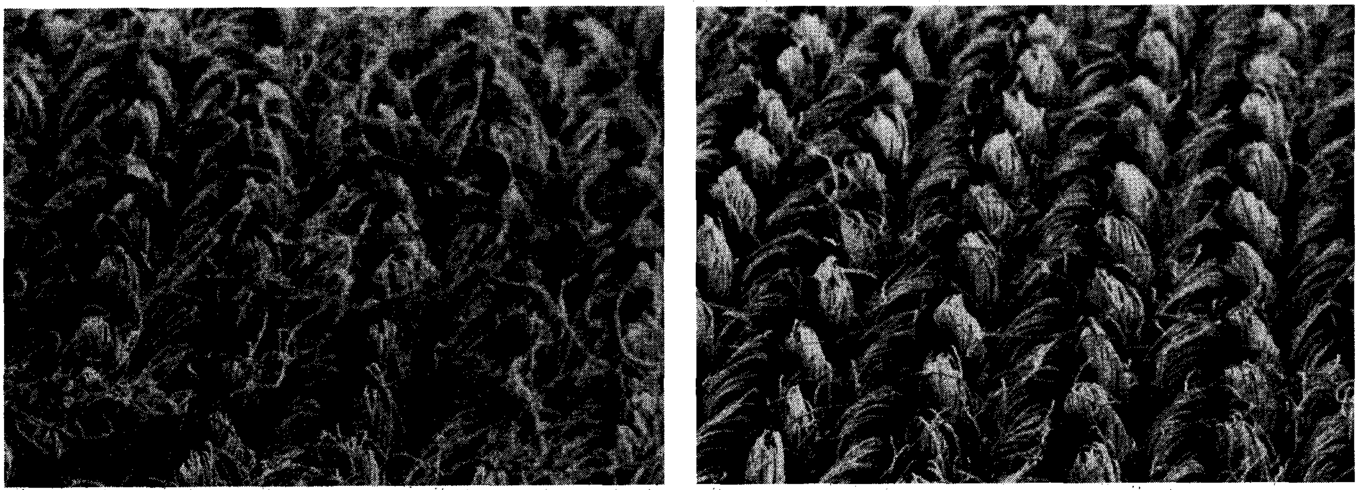

Fig. 1. Surface smoothing effect on lyocell as shown by a micrograph from a Scanning Electron Microscope (SEM) untreated (left) and cellulase treated (right). Photographed at 20X magnification.

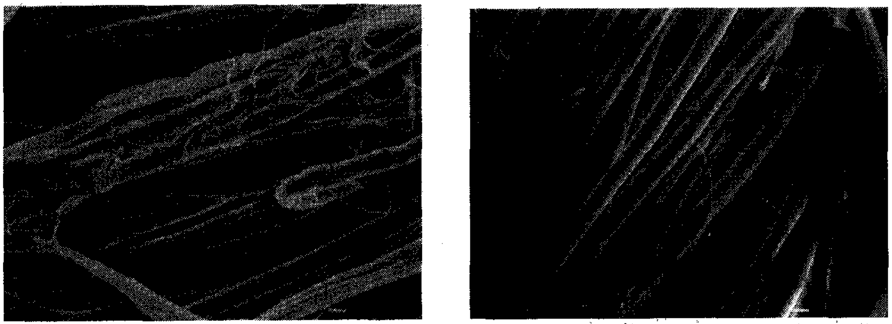

Fig. 2. Surface modification of lyocell of untreated (left) and cellulase treated (right), as viewed by SEM at 100X magnification.

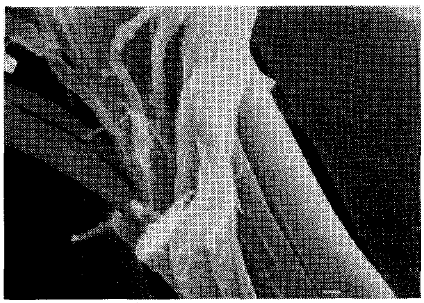

Fig. 3. Lyocell fiber showing primary fibrillation as viewed by a SEM at 500X magnification.

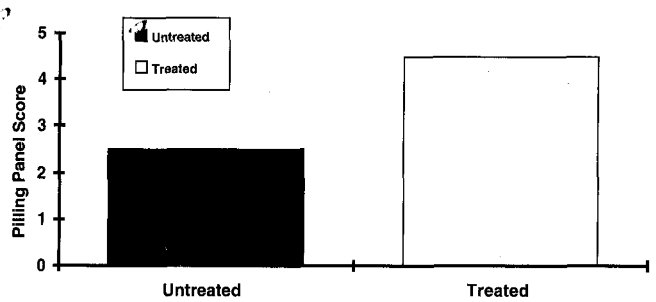

Fig. 4. Pilling tendency following cellulase treatment. The fabrics were panel scored (1=highly pilled to 5=no pills) after 60 minutes of tumbling in a random pill testing device.

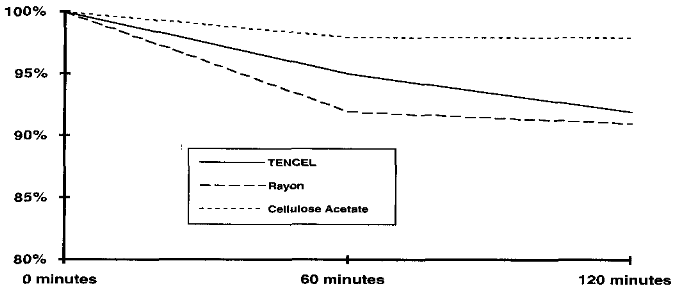

Fig. 5. Compression energy following cellulase treatment. The compression energy and deflection was measured by a Twing-Albert Compression Testing instrument. The trend of the compression energy over the cellulase treatment time is reported as the average of at least five measurements from several representative test fabrics.

the compression energy. The data on lyocell and cellulose acetate correlates well with the respective flex stiffness data and the reduction in weight loss. The compression energy following ten launderings of treated versus untreated rayon supported the observation that the treated rayon felt softer than the untreated laundered rayon.

Enzymes work by cleaving surface fibers which results in some fabric weight loss. In commercial applications, the process is optimized to minimize fabric weight loss while achieving the desired benefit. The weight loss is also highly dependent on which enzyme is used, the fabric construction, and the process used. Generally, a 5% fabric weight loss is needed to optimally modify the surface which is achieved within approximately 60 minutes on lyocell and rayon, see Fig. 6.

Weight loss following cellulase treatment indicates the propensity that the enzyme has for hydrolyzing the particular cellulosic fabric. There is a strong correlation between treatment time and weight loss, as well as treatment dose and weight loss. As a result, the benefits of cellulase treatment are largely controlled by adjusting the treatment time and dose parameters along with the degree of mechanical action provided. Appropriate levels of hydromechanical action will also help control fabric weight loss while optimizing benefits.

Cellulase treatment was most effective on lyocell, but at equal doses, rayon showed similar benefits requiring only slightly longer processing times than lyocell. Again, there was little evidence that cellulase was acting on the cellulose acetate fabrics since there was no significant weight loss even after 180 minutes of cellulase treatment. This evidence for enzyme activity is corroborated by the following strength loss data.

Fabric strength loss is a function of fabric weight loss following enzyme treatment. Fig. 7 indicates that for every percent of weight loss, there is nearly a 2% reduction in the fabric strength. As with fabric weight loss, the strength loss is dependent on the enzyme used, the fabric construction parameters—for example, yarn twist—and the process or equipment used. In commercial processes, lubricants are used following enzyme treatment which often increase the fabric strength above the fabrics original tensile strength.

Fig. 8 shows that cellulase treated fabrics are softer and show less surface fuzzing than untreated fabrics. These differences become more marked as the number of launderings increases. There are also noticeable differences in fabric brightness and in the tendency to pill following laundering. Both of these attributes are related to the tendency to fuzz following ordinary wash and wear cycles. Thus, cellulase treatment produces lasting benefits in softness, controlling pilling and in the maintenance of color and surface appearance. These benefits from enzyme treatment are incremental to benefits associated with auxiliary finishing agents.

Summary

Cellulase treatment of man-made cellulosics represents an extension of work done previously demonstrating the utility of cellulase modification of natural fiber fabrics. Some tangible effects of cellulase treating man-made cellulosic fabrics were shown.

- The benefits indicated are—softening, defuzzing, depilling and pill prevention, improved drapeability and improved surface appearance after multiple launderings.
- Cellulase treatment performed best on lyocell followed closely by rayon. Cellulase had little effect on acetate under the conditions tested.
- The benefits of cellulase treatment are long lasting.

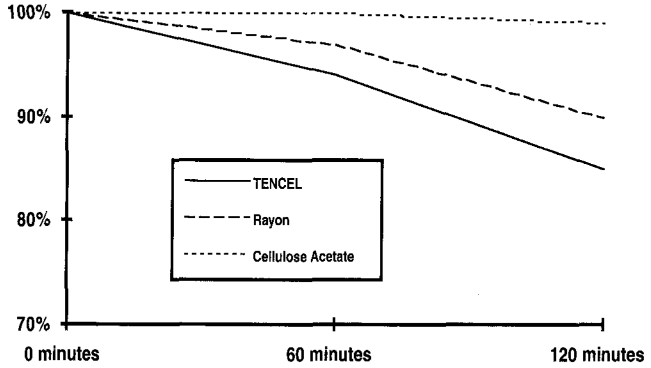

Fig. 6. Fabric weight following cellulase treatment. The fabric weight was taken as the average of several representative test fabrics after processing for 30, 60 and 120 minutes.

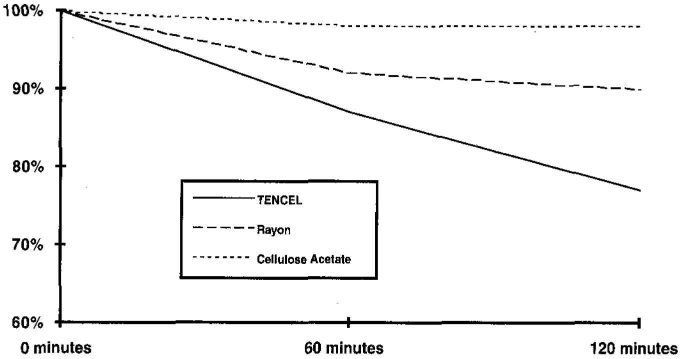

Fig. 7. Tensile strength following cellulase treatment. The tensile strength was taken as the average warp and fill strength of several representative test fabrics after processing for 30, 60 and 120 minutes.

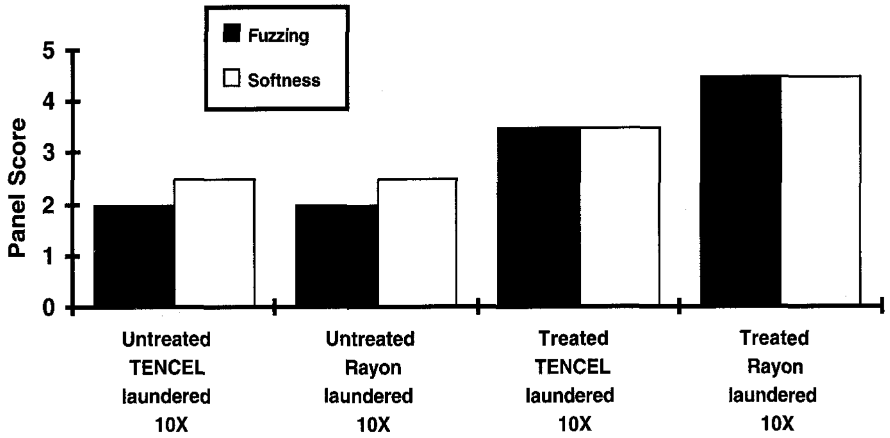

Fig. 8. Panel score for surface fuzzing and softening following multiple launderings. The cellulase treated and untreated fabrics indicated were home laundered (according to AATCC Test Method 143-1984) in a warm wash cycle with AATCC standard detergent and tumble dried with low heat.

Enzyme treatment of lyocell reduced its tendency to fibrillate, improved the surface smoothness, softness, drape and launderability. The surface of rayon was defuzzed, softening was improved particularly following multiple launderings and its tendency to pill was greatly reduced with the use of an enzyme treatment. Cellulase treatment of cellulose acetate suggested no significant benefits under the conditions tested.

Overall, in an industry driven by continual quality improvement, cellulase modification enhances the quality of man-made as well natural fiber fabric. These benefits are long lasting and measurable. The environmental soundness of enzyme processing also supports broader use of cellulase in fabric and garment finishing.

In conclusion, cellulase is not just for cotton anymore. Cellulase effectively improves softness, drapeability, pilling tendencies and post-laundering appearance of rayon and lyocell fabric. Under the conditions tested, little if any benefits were shown on cellulose acetate. The differences in the efficacy of cellulase on various fibers can be explained in part by the amount of non-cellulosic wood pulp-derived matter, the degree of polymerization, the extent and type of chemical modifications and the type and degree of crystalline fiber structure. Finally, these benefits of cellulase treatment should help elevate the standard quality and appeal of man-made fabrics.

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References

1. Hemmpel, W. H., *International Textile Bulletin Dyeing/Printing/Finishing*, Vol. 3, 1991, p5.
2. Olson, Lynne, *American Dyestuff Reporter*, Vol. 77, No. 5, May 1988, p19.
3. Klahorst, Suanne, Akhil Kumar and Margaret Mullins, *Textile Chemist and Colorist*, Vol. 26, No. 2, February 1994, p13.
4. Screws, G. A. and D. M. Cedroni, *Book of Papers*, 1992 AATCC International Conference & Exhibition, Atlanta, p250.
5. Davies, Stan, *Textile Outlook International*, November 1992, p11.
6. Taylor, Jim, "Courtaulds Fibers," A personal communication to Charlie Purtell, Genencor International, August 1992.
7. Rudie, Raye, *Bobbin*, February 1993, p10.
8. Bisaria, S. M. and T. K. Ghose, *Enzyme and Microbial Technology*, Vol. 3, No. 2, April 1981, p91.
9. Joseph, M. S., *Introductory Textile Science*, Fifth Edition, Holt, Rinehart & Winston, New York, 1986, p87.
10. Bellegsen O. and B. A. Tonnensen, *High Polymers*, Vol. V. "Cellulose and Cellulose Derivatives," Wiley, New York, 1971, p151.
11. Betrabet, S. M., *Colourage*, May 1994, p22.
12. Walker, L. P. and D. B. Wilson, *Bioresource Technology*, Vol. 36, 1991, p3.

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SECOND PLACE WINNER: Quebec Section

1993 International Technical Paper Competition

Evaluation of the Post-Bleaching of Knit Fabrics Dyed with Direct, Reactive and Disperse Dyes

ABSTRACT

The traditional scour/bleach/dye process for the preparation of cotton and cotton/polyester knit fabrics was compared with a single bath combined scour-dye process followed by post-bleaching with alkaline hydrogen peroxide in the exhausted dyebath. The post-bleach procedure did not result in the same quality of bleaching as the traditional method but offered considerable savings in time, energy and water. A factorial plan of trials for studying the effects of the process variables on the post-bleaching of the dyed fabrics showed that this operation was successful over a fairly wide range of conditions, so that close control of the process variables was not critical. The major problem encountered was a lack of stability to peroxide of certain dyes for cotton. It was shown that dyeing could easily be translated to the pilot scale and that dyeing to a standard shade was possible.

KEY TERMS

Bleaching
Cotton
Cotton/Polyester
Peroxide
Post-Bleaching

Finding ways to increase productivity has become a constant concern in the textile industries of developed nations due to international competition. Many new dyeing techniques have been developed which minimize costs for water, chemicals and energy. The traditional scheme for preparing and dyeing cotton and cotton/polyester materials involves two or three separate baths for scouring, bleaching and dyeing. In each separate process, the bath must be heated and the treated fabric rinsed prior to the next step. Such a sequence can be replaced by a process in which the three operations are combined and carried out in a single bath, with large savings of water, energy and time.[1-3]

The objective of this project was to evaluate such a combined process, in which cotton and cotton/polyester knitted fabrics would be simultaneously scoured and dyed, and then bleached after dyeing by addition of alkaline hydrogen peroxide to the exhausted dyebath.

Materials and Equipment

Only two tubular knitted fabrics were examined in this study. The first was a 100% cotton jersey knit (161 g/m^2, grey) and the other a more complex 50/50 cotton/polyester interlock knit fleece fabric (176 g/m^2, grey).

Laboratory scale dyeings were carried out in 125 mL steel pots using a Zeltex Polycolor dyeing machine. The liquor ratio was always 10 to 1 (5.00 g fabric plus 50 mL solution). The dyeing beakers were fitted with addition ports sealed with a rubber septum so that chemicals could be injected with a hypodermic syringe during dyeing. Pilot scale dyeings using a Benz HT140 mini-jet dyeing machine were at a liquor ratio of 12.5 to 1 (2.00 kg fabric with 25.0 L water). Both machines were equipped with Sedo PC1000 microprocessors. When using the mini-jet, the procedures had to be modified. Cooling to 80C was necessary for addition of chemicals since the machine seals automatically above this temperature, and it was not equipped with a high pressure metering pump. Addition of 5 mL of a silicone oil was also needed to suppress foam.

Spectrophotometric and colorimetric data were obtained using a Diano Match Scan II double beam spectrophotometer and in-house software.[4] Tristimulus values and CIELAB data were calculated for illuminant D65 and the 1964 supplementary standard observer.[5] Colorant formulation was done with in-house software[6] based on the Allen algorithm.[7] No attempt was made to generate high precision formulas. Only two calibration dyeings were carried out with each dye using 0.20 and 0.40% of dye based on the weight of pre-bleached fabric.

The breaking strength of the fabrics was determined with the Instron Model TTD (Series 3025) using 0.5x2.5 inch strips cut perpendicular to the wale direction. A complete stress versus strain record was obtained in each case.

A variety of dyebath formulas were used and these are listed in Table I. Commercial names of the dyes are given but do not constitute specific recommendations, since the choice was arbitrary and based on the availability of dyes in the laboratory.

Comparison of Traditional and Post-Bleach Processes

The study began by comparing the traditional scour/bleach/dye process with that in which combined dyeing and scouring was followed by bleaching in the same bath. These will be called the normal and post-bleach processes. The two procedures were examined with and without addition of dyes so that the effects on the fabric whiteness could be evaluated.

For these trials, Formulas A and C (Table I) were used. The post-bleach procedure is shown in Fig. 1, which will be referred to as process 1. In the normal process, the cotton or cotton/polyester samples were scoured (105C, 45 min, 1.0 mL/L Sandoclean PCL, 2.0 g/L NaOH). After two rinses in hot water, they were bleached (95C, 30 min, 5.0 mL/L 30% H_2O_2, 1.0 g/L NaOH, 0.5 mL/L SIFA stabilizer). The fabrics were rinsed in hot water, neutralized with acetic acid and rinsed again. They were then dyed with a mixture of direct (cotton) or direct and disperse dyes (cotton/polyester) according to the scheme in Fig. 1, but without addition of the scouring and post-bleaching chemicals.

Fabric whiteness (process without dyes) was assessed by measurement of the tristimulus values and calculation of the CIE whiteness W_{10}.[5]

$$W_{10} = Y + 800(x_n - x) + 1700(y_n - y)$$

where Y, x and y are the Y tristimulus value and the chromaticity coordinates

Table I. Dyebath Formulas (% dye owf) for the Various Processes

Formula A (Cotton - Green)	
Sirius Supra Yellow GD	0.100%
Sirius Supra Blue GR-LL	0.100%
Formula B (Cotton - Green)	
Sirius Supra Yellow GD	0.100%
Ultrasol Navy BL	0.100%
Formula C (Cotton/Polyester - Green)	
Sirius Supra Blue GR-LL	0.050%
Sirius Supra Yellow GD	0.050%
Resolin Blue H-FBL	0.028%
Samaron Yellow 6GSL	0.050%
Formula D (Cotton/Polyester - Green)	
Ultrasol Navy BL	0.050%
Sirius Supra Yellow GD	0.050%
Resolin Blue H-FBL	0.028%
Samaron Yellow 6GSL	0.050%
Formula E (Cotton/Polyester - Violet)	
Resolin Red F-3BS	0.050%
Foron Navy S-2GRL	0.050%
Sirius Supra Red F-3B	0.050%
Sirius Supra Blue GR-LL	0.050%
Formula F (Cotton/Polyester - Violet)	
Resolin Red F-3BS	0.050%
Foron Navy S-2GRL	0.050%
Sirius Supra Red F-3B	0.050%
Ultrasol Navy BL	0.040%
Formula G (Cotton/Polyester - Brown)	
Resolin Red F-3BS	0.300%
Resolin Blue H-FBL	0.180%
Samaron Yellow 6GSL	0.490%
Sirius Supra Red F-3B	0.140%
Sirius Supra Blue GR-LL	0.210%
Sirius Supra Yellow GD	0.410%
Formula H (Cotton/Polyester - Light Brown)	
Resolin Red F-3BS	0.150%
Resolin Blue H-FBL	0.090%
Samaron Yellow 6GSL	0.250%
Sirius Supra Red F-3B	0.070%
Ultrasol Navy BL	0.090%
Sirius Supra Yellow GD	0.200%
Formula I (Cotton/Polyester - Green)	
Resolin Blue H-FBL	0.060%
Samaron Yellow 6GSL	0.050%
Drimarene Navy K-2B	0.070%
Drimarene Golden Yellow K-2R	0.080%
Formula J (Cotton/Polyester - Violet)	
Resolin Red F-3BS	0.050%
Foron Navy S-2GRL	0.050%
Procion Blue H-ERD	0.088%
Procion Red H-EXL	0.094%
Procion Yellow H-EXL	0.016%
Formula K (Cotton/Polyester - Green)	
Resolin Blue H-FBL	0.041%
Resolin Red F-3BS	0.009%
Samaron Yellow 6GSL	0.067%
Cibacron Blue F-R	0.090%
Cibacron Yellow F-4G	0.148%
Formula L (Cotton/Polyester - Green)	
Resolin Blue H-FBL	0.028%
Samaron Yellow 6GSL	0.050%
Kayacelon React Dark Blue CN-R	0.090%
Kayacelon React Yellow CN-ML	0.100%

of the sample, respectively, and x_n and y_n are the chromaticity coordinates for the perfect diffuser, both calculated for illuminant D65 and the 10° standard observer. The results are shown in Fig. 2. For the processes carried out with dyes, samples were taken at each stage of the procedures and colorimetric and strength tests were conducted. As expected, in trials without addition of the dyes, the post-bleach process did not give the same degree of fabric whiteness as the traditional three-bath process. The alkaline scour of the normal process gave more effective fabric cleaning than the neutral scour-dye process of the post-bleach procedure. For identical dye formulas, the colors of the final samples from the normal and post-bleach procedures were not the same. Comparison of samples taken before post-bleaching with the final normal process sample showed visible color differences (cotton, $E^*_{ab} = 3.3$; cotton/polyester, $E^*_{ab} = 2.5$). The dyeings on both cotton and cotton/polyester were visibly weaker and yellower after post-bleaching. With the sample taken before post-bleaching as standard, the bleached dyeings gave $E^*_{ab} = 9.1$ for cotton and $E^*_{ab} = 5.7$ for cotton/polyester. This was mainly a consequence of the bleaching of the blue direct cotton dye in the mixture. The post-bleaching process did not weaken the strength of the fabrics in any significant way because of oxidation of the cotton. Good dyebath exhaustion was obtained—a key requirement for the post-bleaching procedure.

First Runnerup

THE Quebec Section won runnerup honors in AATCC's 1993 Intersectional Technical Paper Competition in Montreal with its study on the post-bleaching of cotton and cotton/polyester knit fabrics dyed with direct, reactive and disperse dyes. Quebec has won first place twice, second once and third once.

The post-bleach process was then repeated on both fabrics using Formulas B and D (Table I), for which the blue direct cotton dye, showing a lack of resistance to bleaching, was replaced by the same amount of the more resistant Ultrasol Navy BL. The colorimet-

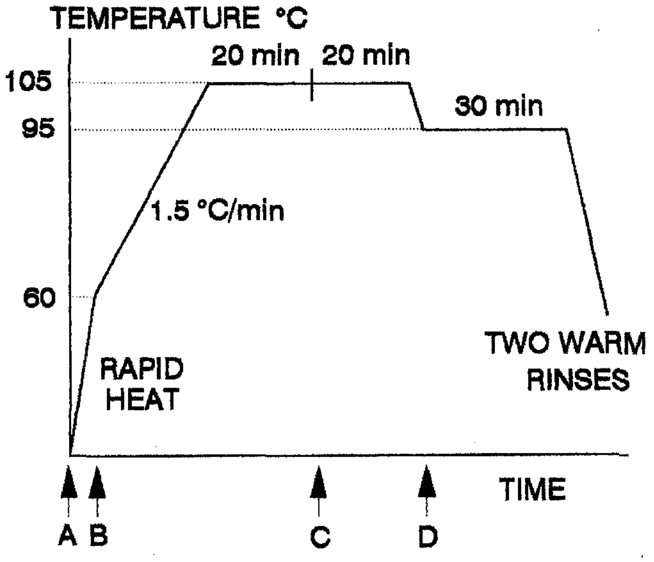

Fig. 1. *Dyeing scheme for the post-bleach procedure. A: add dyes and 1.0 mL/L Sandoclean PCL. B: enter fabric at 60C. C: add 20 g/L salt. D: add 5 mL/L 30% H_2O_2, 1.0 g/L NaOH and 0.5 mL/L SIFA stabilizer.*

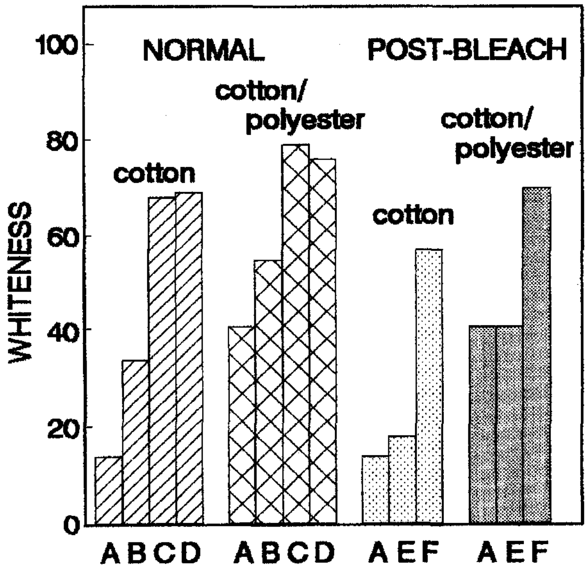

Fig. 2. Values of fabric whiteness for the normal and post-bleach processes. A: original fabric. B: after scouring. C: after bleaching. D: after mock-dyeing. E: before post-bleaching. F: after post-bleaching.

Table II. Real and Coded Values for the Process Variables

Plan 1: single initial H_2O_2 addition, [SIFA] = 0.5 mL/L, 30 min

	Low	High	Symbol
[H_2O_2] mL/L 30%	2.0 (-1)	8.0 (+1)	H
[NaOH] g/L	0.4 (-1)	2.0 (+1)	C
Temp. (C)	80 (-1)	98 (+1)	T

Plan 2: [H_2O_2] = 8 mL/L, [NaOH] = 0.4 g/L, 98C

	Low	High	Symbol
[SIFA] mL/L	0 (-1)	0.5 (+1)	S
Time, min	30 (-1)	48 (+1)	t
Metering H_2O_2	no (-1)	yes (+1)	M

ric data showed that this dye combination gave a somewhat darker and bluer shade, but had little change in hue on post-bleaching. The dyeings became somewhat lighter on post-bleaching because of the effect on the base fabrics.

Process Optimization

In order to select optimum values for the many process variables, their influence on some properties of the bleached fabric and the bath (process responses) was examined. The measured process responses were:

- The degree of whiteness of the fabric, W_{10}.
- The color change of the dyed sample on post-bleaching, CIELAB E^*_{ab}, which gave an indication of the stability of the dyes to alkaline hydrogen peroxide solution.
- The percentage of peroxide consumed (P%) was calculated by titration of the H_2O_2 in the initial and final bleaching solution with standardized potassium permanganate solution in the presence of sulfuric acid.[8]
- The breaking strength of some samples was determined to ensure that bleaching did not unduly weaken the material as a consequence of cellulose oxidation.

Dyebath Formulas B and D (Table I) were used with dyeing and post-bleaching conditions as described for process 1 (Fig. 1).

In process optimization, a factorial design of the trials is normally used.[9] Two separate plans were followed in this case. In both, three process variables were selected for study at two different levels, the other variables being held constant. The high and low values of the process variables studied were expressed as coded values (+1 or -1). A value of +1 shows that a variable had the higher value of the two, and -1 the lower value. The two factorial plans and the values of the process responses are given in Tables II and III.

The breaking strength was measured for all samples submitted to the most severe conditions in plan 1. Post-bleaching did not adversely affect the fabric strengths.

The results of the factorial plan were analyzed by the statistical procedure described by Montgomery.[9] The results are expressed in terms of equations giving the anticipated value of the response in terms of each of the process variables, in the form of coded values (+1 or -1) multiplied by a calculated coefficient. The values of the various coefficients give the magnitude of the effect of each process variable on the average value of the response and the effects of interactions between variables; e.g.,

$$
\begin{aligned}
E^* = E^*_{av} &+ a_1H \\
&+ a_2C + a_3T + a_4HC \\
&+ a_5HT + a_6CT + a_7HCT
\end{aligned}
$$

Tables IV and V give only the values of the coefficients a_1 to a_3 and no values for those coefficients indicating the extent of interactions between variables (a_4 to a_7).

The data in Table IV show that the degree of color change on post-bleaching (E*) is influenced mainly by the concentration of caustic soda and the temperature (coefficients a_2 and a_3). Unfortunately, decreasing the levels of these two variables also decreases the degree of cleaning of the fabrics (lower values of W_{10} in the absence of the dyes). As expected, peroxide consumption was greater at higher temperatures and caustic concentrations. As always, bleaching is a compromise. In the case of the post-bleach process, the desired level of bleaching of the fabric must be balanced against the possible loss of color.

Table V shows that the use of the stabilizer was not of particular value (coefficient a_1). Since continuous metering of the peroxide was not possible with the laboratory dyeing machine, metering was simulated by four equal additions of 25% of the total peroxide required for bleaching at 0, 25, 50 and 75% of the full bleaching time. This resulted in low peroxide consumption and gave a somewhat lower whiteness

Table III. Factorial Plans and Process Responses

Plan 1 (S, t and M constant)						Plan 2 (H, C and T constant)					
Variables			Responses			Variables			Responses		
H	C	T	E*	W_{10}	P%	S	t	M	E*	W_{10}	P%
Cotton											
-1	-1	-1	1.7	42	23	-1	-1	-1	3.2	56	65
1	-1	-1	2.3	45	62	1	-1	-1	2.9	54	65
-1	1	-1	2.7	55	78	-1	1	-1	2.8	56	94
1	1	-1	3.4	57	82	1	1	-1	2.5	57	88
-1	-1	1	3.4	48	89	-1	-1	1	1.9	55	41
1	-1	1	3.2	55	76	1	-1	1	2.4	56	31
-1	1	1	4.7	60	86	-1	1	1	2.1	55	68
1	1	1	4.9	66	82	1	1	1	2.9	53	65
Cotton/Polyester											
-1	-1	-1	2.0	37	50	-1	-1	-1	2.4	69	56
1	-1	-1	2.5	58	40	1	-1	-1	2.0	66	51
-1	1	-1	4.3	64	63	-1	1	-1	2.9	69	95
1	1	-1	4.4	65	63	1	1	-1	2.7	69	85
-1	-1	1	3.6	44	50	-1	-1	1	3.2	62	27
1	-1	1	3.4	62	71	1	-1	1	3.0	59	33
-1	1	1	4.8	66	80	-1	1	1	3.0	60	55
1	1	1	5.5	68	89	1	1	1	2.8	66	63

Table IV. Effects of the Process Variables on the Response for Plan 1

Response	Average Value	Variable Coefficients a_1 H	 a_2 C	 a_3 T
	Cotton			
E*	3.3	0.3	1.3	1.5
W_{10}	54	4.5	12.0	7.5
P%	72	6.5	19.5	22.0
	Cotton/Polyester			
E*	3.8	0.3	1.9	1.0
W_{10}	58	10.5	15.5	4.0
P%	63	5.0	21.0	18.5

Table V. Effects of the Process Variables on the Response for Plan 2

Response	Average Value	Variable Coefficients a_1 S	 a_2 t	 a_3 M
	Cotton			
E*	2.3	0.2	0.0	-0.5
W_{10}	55	-0.5	0.0	-1.0
P%	65	-4.7	28.4	-26.8
	Cotton/Polyester			
E*	2.8	-0.3	0.2	0.5
W_{10}	65	0.0	2.0	-6.5
P%	58	-0.2	32.9	-26.9

(coefficient a_3). Clearly, if peroxide is to be metered into the bleaching bath, sufficient time must be allowed for the peroxide to act on completion of metering. The overall bleaching time did not have a pronounced influence on E* and W_{10} (coefficient a_2).

These data were useful for evaluating the effects of the various process variables on the post-bleach operation. Each trial represents only a single experiment. A full statistical analysis was not attempted since reproducibility of the trials was not evaluated. The data therefore should not be over-interpreted.

Dye Stability

Early in the project, it was apparent that the success of post-bleaching was going to be dependent on the stability of the dyes on the fabrics to treatment with the alkaline peroxide bleaching solution. In the comparison of the normal and post-bleach procedures, Formulas A and C were not satisfactory because of the instability of the blue direct dye. This is not an indicator of poor quality but a characteristic of the specific chromophore. When this dye was replaced by one with a more stable chromophore, the result was much better (Formulas B and D).

In the post-bleaching process some color change is inevitable even if the dyes are completely resistant to the alkaline peroxide solution. This arises because of the bleaching of the base fabric and results in an increased value of L*. Even with dyes exhibiting slight sensitivity to alkaline peroxide solution, some change or loss of color on bleaching would be acceptable if the change was predictable and reproducible.

To test for dye fading during post-bleaching, dyeing trials in the laboratory are necessary. Dyeings can be carried out using the post-bleach procedure and color difference measured. Alternatively, dyeings can be prepared on pre-bleached fabric using the normal dyeing method and then treated with alkaline peroxide solution. We preferred this latter method, since it minimized any color change during post-bleaching arising from the destruction of the colored impurities of the cotton.

The stability to bleaching of the disperse dyes was assessed in aqueous dispersion by heating the dye (0.20 g/L) with H_2O_2 (10.0 mL/L, 30%) and NaOH (1.0 g/L) at 90C for 15 minutes. Transmission spectra were recorded on samples of the aqueous dispersion (10 mL) diluted with acetone (to give 100 mL) before and after treatment with the peroxide. All but two of the nine tested dyes were stable (less than 2% decrease in absorbance at the wavelength of maximum absorption). Foron Navy S-2GFL gave a somewhat increased absorbance and Samaron Blue FBLN was 14% weaker after treatment. It was assumed that the disperse dyes absorbed in polyester would be stable to post-bleaching because of the inability of the inorganic chemicals to penetrate into this hydrophobic fiber (cf. reduction clearing).

Direct and reactive dyes in aqueous solution and on cotton were much more sensitive to bleaching by alkaline peroxide. Dyeings on the scoured and bleached cotton knit (1.0% owf) were prepared by the suppliers' recommended procedures. The degree of fading upon bleaching in solution, and on the fabric, was assessed by spectrophotometric methods. For the dyed fabric samples, the Kubelka-Munk K/S values given by

$$K/S = (1 - R)^2/2R$$

were determined at the wavelength of

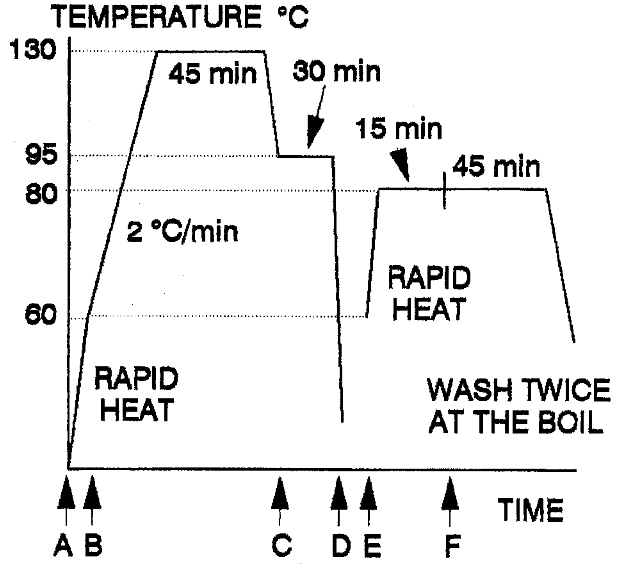

Fig. 3. Process 2 for the dyeing of cotton/polyester. A: add disperse dyes and 1.0 mL/L Sandoclean PCL. B: enter fabric at 60C. C: add 5 mL/L 30% H_2O_2, 1.0 g/L NaOH and 0.5 mL/L SIFA stabilizer. D: rinse and refill with a fresh bath. E: add reactive dyes and 40 g/L salt. F: add 10 g/L soda ash.

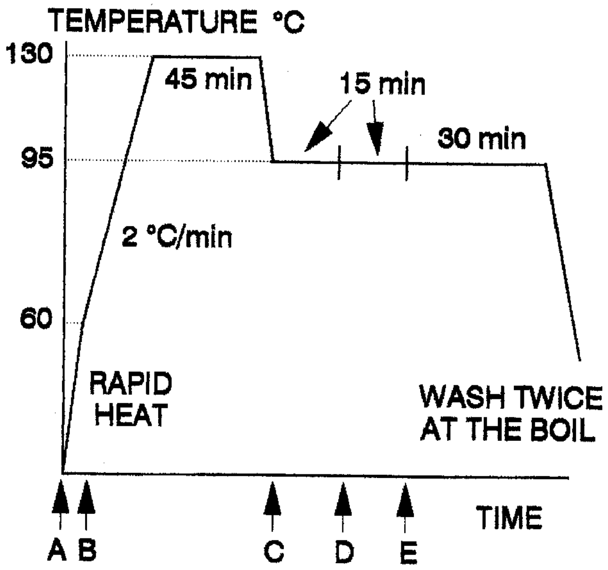

Fig. 4. All-in-one process 3 for dyeing cotton/polyester. A: add dyes and 1.0 mL/L Sandoclean PCL. B: enter fabric at 60C. C: add 40 g/L salt. D: add 1.0 g/L NaOH. E: add 5mL/L 30% H_2O_2 and 0.5 mL/L SIFA stabilizer.

minimum limiting reflectance (R) both before and after bleaching with a solution of H_2O_2 (10.0 mL/L, 30%) and NaOH (2.0 g/L) at 95C for 30 minutes. This gave a measure of the change in K/S; i.e., (K/S). The bleaching of the same dyes was also examined in solution. For this, the dye solution (20.0 mg/L) was treated with H_2O_2 (0.15 mL/L, 30%) and NaOH (0.02 g/L) at 100C for 15 min. These conditions resulted in partial bleaching which could be readily evaluated. The transmission spectra of the solutions were recorded before and after bleaching and the values of the absorbance at the wavelength of minimum transmission were calculated to give the change in absorbance A.

It was thought that there would be a correlation between the stability of the dye on the fiber and its stability in solution. Such a correlation would have allowed much more efficient pretesting of dyes since the solution tests can be conducted much more rapidly than tests on the fabric. The data for the reactive dyes was totally irregular—certain dyes being much more stable in solution than on the fiber and vice versa. This result merits further study. In general, most of the limited number of direct dyes examined were less stable than the reactive dyes, and there was a rough linear correlation between - (K/S) and the - A (regression coefficient = 0.87) if the deviant point (Ultrasol Yellow 3-LG) was excluded. The better stability to bleaching of this dye in solution is probably related to the disappearance of the absorbance maximum at 410 nm while bleaching (inaccurate estimation of A).

For the moment, it can only be recommended that the selection of dyes for the post-bleach process be based on tests of actual dyeings and evaluation of changes in strength and shade, particularly for reactive dyes.

Dyeing Cotton/Polyester with Reactive and Disperse Dyes

A few simple trials were conducted on post-bleaching cotton dyed with reactive dyes. This is not a particularly recommended procedure because some reactive dyes cannot withstand post-bleaching at above 80C. In addition, exhaustion with some reactive dyes is far from complete and much of the peroxide is consumed by oxidation of the residual dye.

The grey cotton/polyester knit was dyed with Formula I using a modified process 2 (Fig. 3). After post-bleaching, the bath was neutralized with acetic acid but was not replaced. The reactive dyes were then applied at 40C rather than 80C, using 20 g/L salt and 7.5 g/L soda ash. A similar dyeing was carried out without addition of H_2O_2. The bleached sample ($L^* = 62.5$, $a^* = -13.6$, $b^* = 4.3$) was lighter but on shade ($E^* = 5.9$, $H^* = 0.0$ versus the unbleached sample). In this process, a single bath was used so that there was some residual peroxide in the bath when adding the reactive dyes after neutralization. The dyeings were found to be somewhat unlevel, probably because of redeposition of oil from the emulsion when cooled to the low dyeing temperature.

Two different approaches for the application of the disperse and reactive dyes to the cotton/polyester knit were compared. The reactive dyes selected were those giving good bath exhaustion. In the first process (process 2, Fig. 3) a fresh bath was used for the final step in which the reactive dyes were applied at 80C with salt (40 g/L) and fixed with soda ash (10 g/L). The second (process 3, Fig. 4) was an all-in-one process in which the disperse and reactive dyes were applied in neutral solution at 130C for 45 minutes. Dyeing trials were carried out with the cotton/polyester fabric using these procedures, both with and without addition of the H_2O_2. In this way, the effect of bleaching on the fabric color could be evaluated. At this stage the objective of matching two standard shades using formulas J and K was set.

The results showed that the two-bath process (process 2), with a post-bleach before the application of the reactive dyes was quite successful, considering that formulation was based on only two calibration dyeings for each dye with pre-bleached white fabric. The all-in-one process (process #3) did not give significant color differences with post-bleaching, but matching the standard shade was more difficult without corrections. This again may be a problem of the original formulations.

A pale green shade was developed specifically (formula L) for the all-in-one dyeing method (process 3). This formula and procedure were used on both the laboratory (5 g) and pilot scales (2 kg). After post-bleaching, there was very little change in hue, but the pilot scale dyeing was slightly paler than the laboratory dyeing. Two parts of the dyeing procedure were modified because of the lack of a high pressure pump capable of metering chemicals into the mini-jet when it was pressurized. The salt (20 g/L) was added at the beginning of dyeing cycle, and for post-bleaching the exhausted bath was cooled to 80C for addition of the peroxide and caustic before re-heating to the bleaching temperature of 95C. This all-in-one procedure was successful and there was no problem in scaling up using the modified method.

Table VI. One-Bath Dyeings of Grey Cotton/Polyester using Process 1

Samples Taken Before and After Bleaching

Sample	L*	a*	b*	E*	H*
Formula E (Cotton/Polyester - Violet)					
Before	52.6	15.6	-14.2		
After	57.5	19.0	-13.1	6.0	3.0
Formula G (Cotton/Polyester - Brown)					
Before	36.4	5.7	5.2		
After	38.9	6.6	7.1	3.1	0.7
Formula F (Cotton/Polyester - Violet)					
Before	50.8	15.5	-16.5		
After	56.1	15.4	-16.8	5.3	0.3
Formula H (Cotton/Polyester - Light Brown)					
Before	44.8	5.1	8.3		
After	48.1	3.7	9.0	3.6	1.6

Table VII. Color Loss Occurring on Severe Washing

	E*	H*
Formula K (Cotton/Polyester - Green)		
Process 2		
Unbleached	1.1	0.5
Post-Bleached	0.4	0.1
Formula E (Cotton/Polyester - Violet)		
Process 1		
Unbleached	3.1	1.1
Post-Bleached	2.5	0.9
Formula G (Cotton/Polyester - Brown)		
Process 1		
Unbleached	5.2	0.1
Post-Bleached	4.1	0.5
Formula F (Cotton/Polyester - Violet)		
Process 1		
Unbleached	4.4	0.3
Post-Bleached	3.4	0.2
Formula H (Cotton/Polyester - Light Brown)		
Process 1		
Unbleached	4.8	0.2
Post-Bleached	3.4	0.2

Post-Bleach Trials with Other Dyes

Several other combinations of direct and disperse dyes were applied to the cotton/polyester fabric using the post-bleach procedure (process 1, Fig. 1). The formulas and colorimeter data are given in Table VI.

Pilot Scale Dyeings

Formula D, a green direct/disperse combination (Table I), was run on a pilot scale according to process 1 (Fig. 1), modified by cooling to 80C before the additions of salt, H_2O_2 and NaOH. The final fabric had coordinates of $L^* = 62.5$, $a^* = -15.1$ and $b^* = 4.8$. When these were compared with those of the laboratory dyeing, $E^*_{ab} = 1.1$ and $H^* = 0.5$. Thus, process scale-up was successful.

Fastness to Washing of Post-Bleached Dyeings

A number of the dyed samples which had been prepared using a post-bleach process were soaped twice at 80C for 30 min at a liquor ratio of 10 to 1 using 0.5 mL Sandoclean PCL. The loss of color was evaluated by colorimetric measurements and reported as the E^*_{ab} and H^*_{ab} values, using the original unwashed dyeings as standards. Samples, which were cut before post-bleaching and rinsed, were also washed by the same procedure and evaluated in the same manner. The results are given in Table VII and show that post-bleaching gave improved fastness to severe washing in every case. It is thought that this is partly because post-bleaching clears the residual disperse dye from the cotton fibers.

Conclusions

Post-bleaching of dyeings is a viable process if the selected dyes have good exhaustion and have either been shown to be stable to alkaline peroxide, or they give a minimal and reproducible loss of color after bleaching. No serious difficulties were encountered in formulation or in scaling up the procedures. Prior laboratory tests are advised to establish adequate dyebath formulas and to select suitable dyes. The factorial plan analysis showed that there is considerable latitude in the choice of post-bleaching conditions but the fabrics do not attain the degree of cleanliness achieved using the traditional scour/bleach/dye process. The use of this type of post-bleaching in the dyehouse, for those fabrics and shades needing some bleaching, offers savings in time, energy and water. Based on current Canadian practice, it is estimated that savings of $0.01 for water, $0.05 for energy and $0.03-0.04 for labor per kg of goods treated can be obtained. In addition, reduction clearing of residual disperse dyes from the cotton fibers is not necessary.

Committee Members

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References

1. Rocha Gomez, J. I. N. and G. M. Vasconcelos Almeida, *Journal of the Society of Dyers and Colorists*, Vol. 102, No. 11, November 1986, p349.
2. Walker, B., *American Dyestuff Reporter*, Vol. 77, No. 8, August 1988, p48.
3. Sharma, P. C., *Colourage*, Special Issue, 1991, p25.
4. Broadbent, A. D. and B. Côté, ChromUS Colorimetry Calculation Software, Université de Sherbrooke, 1990.
5. *Colorimetry*, 2nd Edition, International Commission on Illumination, CIE Publication No. 15.2, Vienna, 1986.
6. Broadbent, A. D. and K. Belkacemi, COLFORM II Colorant Formulation Software, Université de Sherbrooke, 1992.
7. Allen, E., *Journal of the Optical Society of America*, Vol. 56, 1966, p1256.
8. *AATCC Technical Manual*, Vol. 66, 1991.
9. *Design and Analysis of Experiments*, 3rd Edition Montgomery, D. C., John Wiley and Sons, New York, 1991.