

Aqueous Processes for Dyeing Generic, Unmodified Polypropylene Fiber

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ABSTRACT

Acid leuco vat dyeings of polypropylene (PP) fabrics in combinations of a trichromatic series of colorants (red, yellow and blue) plus an orange were performed in order to determine the compatibility of the component colorants in the developed single stage, batch exhaust dyeing process reported earlier.[1, 2] Cross-section micrographs of dyed fibers revealed the absence of “ring-dyeing”. Tensile tests and X-ray crystallinity results confirmed that the developed dyeing process did not significantly alter the tensile strength and modulus of the dyed PP textiles. PP fabrics dyed with simulated, continuous acid vat dyeing processes (pad-steam and pad-dry heat) demonstrated good color yields and levelness with adequate fastness to crocking, washing and dry cleaning.

INTRODUCTION

Since the advent of stereo-regular isotactic polypropylene (PP), the fiber has been used in many industrial applications as well as in carpets and apparel due to its high degree of crystallinity, good handle, strength and a sufficient melting point for normal use [1]. The potential commercial importance of relatively inexpensive, unmodified polypropylene (PP) fiber in the carpet and textile industries has led to research to develop an aqueous dyeing process for the highly-hydrophobic fiber, consistent with the established coloration processes in use for other high-volume fibers (cotton, nylon, polyester and acrylic). Despite substantial research conducted around the globe, a commercially viable and sustainable aqueous dyeing process of PP based on demand-activated manufacturing has not been realized.

PP offers the advantages of exceptionally low price, good strength and aesthetic properties, along with many other desirable characteristics of a textile/carpet fiber, thus creating the impetus for manufacturing from it a variety of materials such as towels, floor coverings, sportswear and select technical products. Due to its nonpolar and hydrophobic nature, most of the current PP fiber is colored by melt pigmentation in spinning. This route of coloration gives excellent fastness properties during end use; however, it restricts the producer in fulfilling the changing fashion demands of the market and creates colored inventories subject to market season whims. Alternative routes for coloring PP fiber exist in which the fiber can be rendered dyeable by means of post-modification, e.g., creating active sites for dye association, or by adding hydrophilic comonomers to the polymer backbone during polymerization. However, each route has adverse effects on the mechanical properties and costs of the fiber. The development of a truly aqueous process for dyeing PP in its generic, unmodified form is thus of significant importance vis-à-vis the rising market demand for this relatively inexpensive fiber.

A viable process for batch exhaust vat dyeing unmodified PP, spun yarn fabrics was developed and reported earlier.[2] The main findings of the earlier research were focused on the development of a trichromatic series of colorants (red, yellow and blue) plus an orange for batch dyeing of PP fabrics using only single colorants. The reported process was further optimized in order to maximize the dye yield on the fabric. This report is mainly focused on the acid leuco dyeing of PP with combinations of the trichromatic series plus orange colorants, and

development of simulated, continuous dyeing processes to color the unmodified PP fabric.

Theoretical molecular dynamics simulations and solubility parameter (SP) approaches were first utilized to screen potential vat dye candidates for generic PP coloration based on their chemical structures. The correlation between dye exhaustion and the SP for PLA fiber and disperse dyes has been reported by Karst *et al.* [3, 4], who showed that the closer the SP of the dye was to the fiber, the better the exhaustion of the dye. SP was calculated as the square root of the cohesive energy density.

In the case of disperse dyeing of polyester and PP, the low molecular weight dye molecule diffuses into the opened structure of the fibers at high temperatures (above their T_g) and is physically entrapped in the unordered regions of the fiber after cooling. A similar mechanism was projected for acid leuco vat dye diffusion into the solid state structure of PP fiber. This mechanism of dye diffusion involved the solubility of the colorant molecule inside the hydrophobic fiber at elevated temperatures, and therefore acid leuco vat dyes (the solute) which possessed SP's closest to that of the PP fiber (the solvent, SP of ~ 8.1 (cal/cc)^{1/2}), coupled with accompanying low predicted mixing energies (ME's) with PP, were theorized to give greater color yields in high temperature dyeing processes.

Identification of viable vat dye candidates of a trichromatic series (compatible red, yellow and blue colorants) plus an orange based on the developed single-stage, acid leuco vat dyeing process was achieved with adequate fastness properties to washing, crocking and dry-cleaning: C. I. Vats Yellow 2 (SP:15(cal/cc)^{1/2}), Red 1 (SP:16(cal/cc)^{1/2}), and Orange 1 (SP:14.6(cal/cc)^{1/2}) were certified, whereas C. I. Vat Blue 6 (SP:18.6(cal/cc)^{1/2}) was demonstrated to be a marginal, though best available and acceptable, candidate. The compatibility of the above colorants in mixtures was also demonstrated by plotting their rates of dyeing in combination for light, medium and dark shades. C. I. Vats Yellow 2, Red 1, Blue 6 and Orange 1 exhibited good dyeing rate compatibilities in combination. C. I. Vat Blue 1 (indigo) (SP:16.7(cal/cc)^{1/2}) also showed excellent color building and good fastness properties in PP coloration, and is thus a viable "stand alone" colorant to dye PP fabrics in the optimized, single-stage acid leuco dyeing process.

The Kubelka-Munk Equation was utilized to derive K/S values of dyed PP fabrics at the colorants' wavelengths of minimum reflectance):[5]

$$\frac{K}{S} = \frac{(1 - R^2)}{2R} \quad (1)$$

Here, R is reflected light measured at wavelength of minimum reflectance, K is the coefficient of absorption and S is the coefficient of scattering. The K/S value for a given dye is directly proportional to its concentration, so it can be used as a measure of dye strength on a given fabric for that particular dye. The K/S values plotted in Figure 8 were obtained at the wavelengths of minimum reflectance for each dye.

The K/S values were in good agreement with the predicted ME's of acid leuco vat dyes and PP fiber, and with the dyes' calculated SP's.[2] The low SP/ME acid leuco vat dyes (e.g., C. I. Vat Red 1) exhibited superior K/S values/fastness properties on colored PP fabrics than high SP/ME vat dyes (e.g., C. I. Vat Brown 1), indicating that increasing difference of SP between the vat dye and the PP fiber, coupled with a higher ME of the dye-PP blend, results in decreased interactions between the two. For example, PP fabrics dyed with C. I. Vat Brown 1 with its high SP (19.3 (cal/cc)^{1/2}) and predicted ME with PP (46.1 kcal/mole) exhibited a lower K/S value than those colored with the certified vat dyes, all with lower SP's/ME's with PP fiber.[2]

Tensile testing of the acid leuco vat dyed PP fabrics revealed no significant impact of the developed dyeing process on the breaking loads and tenacities of the dyed samples. X-ray crystallinity diffraction patterns confirmed no significant impact of the dyeing process on the solid-state structure of the colored PP fibers. Cross-sectional micrographs of loose, dyed fibers confirmed the absence of ring-dyeing.

Translating the finding of the exhaust batch dyeing research, the developed, simulated pad-steam acid vat dyeing process for generic PP fabrics yielded higher fabric K/S values than the analogous batch dyed fabrics for C. I. Vats Yellow 2 and Blue 1. C. I. Vat Blue 6-dyed fabrics exhibited similar color depths in both the exhaust batch and simulated pad-steam processes. Fabrics dyed with C. I. Vats Orange 1 and Red 1 by the simulated pad-steam process exhibited slightly lower K/S values than analogous fabrics colored in the exhaust batch process.

The developed, simulated pad-dry heat dyeing process for C. I. Vat Red 1 on generic PP produced a fabric with a similar K/S value to that generated by the simulated pad-steam method at analogous pad bath formulations. Vat dyed fabrics produced by both the simulated, continuous pad-steam and pad-dry heat processes exhibited adequate fastness to wet/dry crocking, washing and dry cleaning.

EXPERIMENTAL

Materials

Woven PP fabric made from spun, double-ply PP yarns was obtained from TestFabrics, Inc., and was scoured with AATCC Standard Detergent 1993 solution and thoroughly rinsed with ambient temperature water prior to dyeing. Vat dyes provided by Springs Industries, Inc., Classic Dyestuffs, Mount Vernon Mills and C. H. Patrick Company were used as received. Vat dyes received were in liquid as well as powder form: C. I. Vat Red 1 (powder with dispersing agent filler); Vats Yellow 2, Blue 6 and Orange 1 (aqueous particulate suspensions with dispersing agent filler); and Vat Blue 1 (powder with dispersing agent filler). The purities of the dyes (and thus the percentages of the masses that were fillers) were unknown, as they were not disclosed by the dye manufacturers and were considered proprietary. All of the dyes were thus considered as 100% pure as received when calculating the masses to be added to the various dye baths.

Laboratory grade sodium hydroxide was obtained from Fisher Scientific, Inc., and laboratory grade sodium hydrosulphite was obtained from J. T. Baker Company. Rexan LFDD (nonionic leveling agent) and Barapon C 108 (anionic chelating agent) were provided by Dexter Chemical, LLC.

Dyeing of Unmodified PP Fabrics

Exhaust batch dyeings of unmodified PP fabrics were conducted after further optimizing the method previously reported.[2] A long liquor ratio of 100:1 was utilized to generate an “infinite dyebath,” and thus demonstrate the good affinity of the acid leuco vat dyes for the PP fiber. The major change in the optimized dye method was to conduct the colorant air oxidation step prior to cold rinsing so as to maximize the conversion of the acid leuco dye compounds into the insoluble keto forms. Another change was that the absorbance of the dye solution was measured after adding additional reducing agents (sodium hydroxide

and sodium hydrosulphite) to convert the colorant in the sample to the sodium leuco-vat (dianion) form.

Measurement of Percent Exhaustion Using UV/Vis Spectrophotometry

In preparing calibration curves [6]:

- First 0.1 gm of dye was weighed and diluted with water to make a one liter solution (100 ppm)
- Scanning of a 50 ppm solution from 400 nm to 700 nm wavelength in the UV/Vis spectrophotometer was performed to determine the wavelength of maximum absorbance (λ_{max}). Each time a cuvette filled with distilled water was taken as a reference to the dye solution.
- A 100 ppm dye solution was diluted to 50 ppm, 40 ppm, 20 ppm, 10 ppm and 5 ppm, and each of these concentrations was measured for absorbance at (λ_{max}) using Cary 5G Varian UV/Vis NIR Spectrophotometer.
- All the dye solutions to be measured for absorbance were converted into alkaline leuco form prior to measurement using sodium hydroxide and sodium dithionite at pH (10-12).
- Values of absorbance versus concentration (ppm) were plotted, and by using the regression equations determined from the plots along with measured absorbances at dye cycle time t , the dye concentrations of extracted aliquots of baths were determined.

Percent exhaustion was calculated by [6]:

$$\% \text{ Exhaustion} = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

Here C_o was the initial concentration of the dye in the bath in ppm, and C_t was the reduced concentration of the dye at time t .

Measurement of K/S Values for Vat Dyed PP Fabrics

The Hunterlab Reflectometer Ultrascan XE sensor was standardized using the light trap/standard white tile, and was tested for accuracy before measurements using the diagnostic green tile. D65 as standard illuminant and 10° as standard observer were selected for all the measurements. After the standardization, reflectance values at wavelength of minimum reflectance were measured and K/S values were calculated for the dyed samples. Five readings

were recorded at different points on each of the dyed PP fabrics, and an average of the five readings was compiled to calculate K/S values for each fabric.

Evaluation of Crock Fastness: AATCC Standard Test Method 8-2004

Crock fastness was evaluated using the SDL Electronic Crock Meter by following AATCC Standard Test Method 8-2004 [7]. Dyed specimens taken for this measurement were at least 2"x5" in dimension. Evaluation of the crock fastness rating was performed using AATCC grey scales for staining on the scale of 1 to 5. A rating of '5' was assigned to the sample which exhibited negligible color fading or negligible staining on the white test cloth square.

Evaluation of Wash Fastness: AATCC Standard Test Method 61-2003

Test II A of AATCC Standard Test Method 61-2203 was utilized to evaluate the wash fastness of dyed fabrics expected to undergo repeated low temperature machine washing in the home or in a commercial laundry [8]. The test specimen of 2"x5" was sewn together with the multifiber fabric strip of style # 10 and entered into the glass beaker containing the above solution and the temperature was maintained at 49°C using a thermostat-controlled hot plate. The beakers were covered with the round glass plates to minimize the evaporation of the solution. Stirring was accomplished by a magnetic stirrer. After the soaping treatment, the composite specimen was removed from the beaker and rinsed twice with fresh water, squeezed and finally air dried overnight on the bench. After drying, the specimen was evaluated for wash fastness rating using the grey scale of 1 to 5.

Evaluation of Color Fastness to Dry Cleaning: AATCC Test Method 132-2004

The entire test procedure was conducted inside of a hood. Perchloroethylene (PERC)/detergent mixtures (1% charge/volume at 75 % relative humidity) were prepared [9] using 100 ml of PERC, one drop of water and 1 gm of Perk Sheen 324 (detergent for PERC system supplied by ADCO Inc.) while stirring the contents of the beaker. A 2"x6" specimen was sewn together with the multifiber fabric strip and placed into a beaker containing 100 cc of 1% charge of PERC-detergent mixture together with a magnetic stirrer. The beakers were kept over a thermostat-controlled hot plate, and the temperature of the hot plate was maintained at 30 ±2°C for 45 minutes. The beakers were covered with round glass plates to minimize the evaporation of the solution. After the treatment, the beakers were removed from the hot

plate. The samples were removed from the beakers and placed on a paper towel in a closed hood overnight (>8 hours) to dry. The remaining PERC-detergent solution was placed in a separate closed bottle and labeled as "hazardous waste". After drying, the samples were taken out of the hood, and the fastness ratings were determined using the grey-scales for staining on the various components of the multifiber fabric and changes in color of the dyed fabrics.

Evaluation of Tensile Strength (ASTM: D 2256-97)

Influences of the dyeing process on the tensile strengths of yarns extracted from the greige (standard) and dyed fabrics were determined. Single strand yarn specimens were broken on an Instron Model 5567 tensile tester at a constant rate of elongation (60 mm/minute), and the breaking strengths and the elongations at break were determined for both greige (undyed) and dyed samples [10].

The straight configuration was used in these experiments in which the yarn was clamped into the bottom clamp. After setting up a gage length of 100 mm, the other end of the yarn was clamped into the top clamp. Testing was carried out in standard atmosphere conditions (21 ± 1 °C, 65 ± 2 % RH). Ten measurements were taken for each dyed fabric sample, and an average was then calculated for the comparison to the undyed sample. Breaking tenacity was calculated by:

$$B = \frac{F}{T} \quad (3)$$

B= breaking tenacity in gms/denier

F= breaking force in gms

T= linear density of yarn in denier

Tensile modulus was determined using:

$$\text{Tensile modulus} = \frac{\text{Breaking stress}}{\text{Breaking elongation}} \quad (4)$$

Degree of Crystallinity of Dyed PP Fibers

In order to investigate the effect of the optimized, exhaust batch dyeing process on the solid-state-structure of the PP fiber, Wide-Angle X-ray Diffraction (WAXD) studies were conducted on a Rigaku Micromax-002 WAXS/SAXS system operating at a voltage of 45 kV and a current of 0.66 mA equipped with a Rigaku R-axis IV++ 2-D detection system. The analyses of the diffraction

patterns were performed using AreaMax V. 1.00 and MDI Jade 6.1 software.

Simulated Continuous Pad-Steam Dyeing of Unmodified PP Fabrics

Continuous dyeing processes are commercially well-established, particularly in the carpet and flat woven fabric/towel manufacturing industries. Continuous dyeing allows minimum production time and efficient usage of raw materials and manpower compared to batch dyeing. Vat dyes are currently utilized to color cotton fiber in pad-steam fixation processes in the flat fabric/towel industry, portending the development of an analogous dyeing process for generic PP products [5]. Similarly, the volume dyeing production process in use today for tufted nylon carpet coloration is continuous pad-steam acid dyeing. Future generic PP carpets will therefore need to be processed in a similar manner.

The PP fabrics were dipped into the dye pad and chempad formulations in succession for 2-3 minutes and the excess liquor was then hand squeezed out to achieve a wet pickup (WPU) of ~70%, simulating conventional pad-roller nip operations. The developed, optimized process for simulated, continuous pad/steam coloration of unmodified PP fabric with acid leuco vat dyes was based upon the method first described by Ulrich *et al.*[11]:
Fabric weight: 20 gms

Dye pad:

Amount of dye: 5.7 gm (based on 70% wet pickup and 8% owf)
Albaflow pad 01 (wetting agent of Huntsman Chemical Company): 6 cc of 1% solution (1.2 g/l)
Total weight of dye pad solution: 50 gm

Chempad:

Sodium hydroxide: 28 cc of 1% solution
Sodium hydrosulfite: 5.7 gm
Total weight of chempad solution: 50 gm
The dyeing sequence was:
Dye pad/squeeze to 70% WPU → dry at 100-110°C for 5 minutes → chempad/squeeze to 70% WPU → steam for 15 minutes → cold rinse → soap → wash → air dry
The evaluations of K/S values and fastness properties of the dyed fabrics were performed as described in the experimental section.

Simulated Continuous Pad-Dry Heat Dyeing of Unmodified PP Fabrics

Existing Thermosol[®] process lines in current use for continuous disperse dyeing of polyester in 100% and blend constructions were deemed suitable for adaptation of a continuous pad-dry heat process for the acid leuco vat dye coloration of generic PP fabrics, albeit at a much lower oven temperature than that used for sublimation disperse dyeing of polyester (>200°C) and with the pre-drying step after the dye pad eliminated or by-passed. The maximum temperature exposure recommended for PP fiber (MP of ~169°C) is 130°C. [12].

The optimized, single-pad bath process was based on the concept described by A. V. Mishchenko *et al.* [12], who demonstrated that dry heat treatment (140°C) accelerates the diffusion of acid leuco vat dyes into the amorphous regions of unmodified PP fiber. The optimized dyeing conditions were:

Fabric weight: 10 gms
Amount of dye: 2.85 gm (based on 70% pickup and 8% owf)
Sodium hydroxide: 14 cc of 1% solution
Sodium hydrosulfite: 2.85 gm
Albaflow pad 01 (wetting agent of Huntsman Chemical Company): 3 cc of 1% solution (1.2 g/l)
Total weight of vat acid pad solution: 25 gm
The PP fabric was dipped into the vat acid solution for 2-3 minutes and hand squeezed to achieve a WPU of 70%. The dyeing sequence was:
Vat acid pad/squeeze to 70% WPU → oven exposure at 130°C for 10 minutes → cold rinse → soap → wash → dry.

RESULTS AND DISCUSSION

Cross-Sectional Micrographs of the Dyed Specimens

The PP fabric was batch exhaust dyed with single acid leuco vat colorants by the method reported earlier.[2] Cross-sections of yarns pulled from the fabric were examined to assess through-yarn dye uniformity via microtoming. The cross-sectional pictures confirmed dye diffusion through the diameter of individual fibers colored on the outer surfaces of the yarns, i.e., “ring dyeing”, was not evident, but not all of the fibers through the center of the yarn diameters were uniformly colored (*Figure 1*).

Poor dye bath circulation and pumping pressure through the yarns of the tightly-woven, multi-layered PP fabric in the Roaches lab dyeing machine were suspected as the causes of the through-yarn dye non-uniformity. To assess the theory, loose, generic PP fiber stock was obtained from FiberVisions, Inc. The fiber stock was colored on the Roaches machine under the optimized batch acid leuco vat dyeing conditions, and cross-sectional pictures were made of the dyed fiber bundles. The cross-sectional pictures of the loose, dyed fibers revealed excellent through-diameter penetration of the dye in all of the individual fibers. The results confirmed that uneven dyeing of individual fibers mainly in the center of yarns in the tightly-woven PP fabric was due to inadequate dye liquor circulation through the multi-layer (4-5) woven fabric structure mounted on the cores of the Roaches Colortec Lab Dyeing Machine.

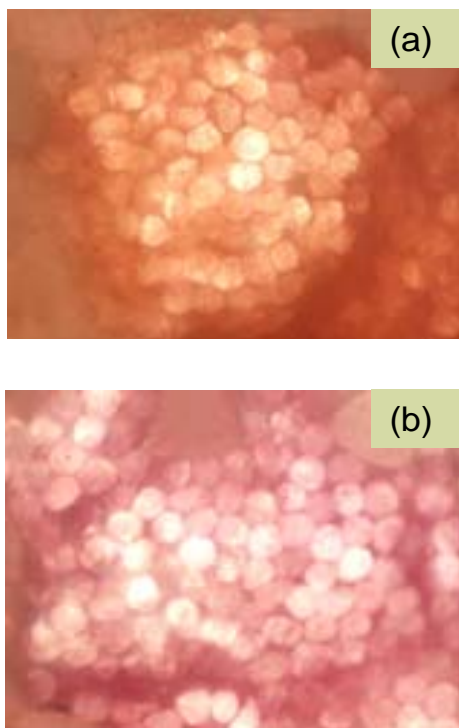


FIGURE 1. Cross-Sections of PP Yarns Extracted from Woven Fabrics Dyed with: (a) C. I. Vat Orange 1; and (b) C. I. Vat Red 1

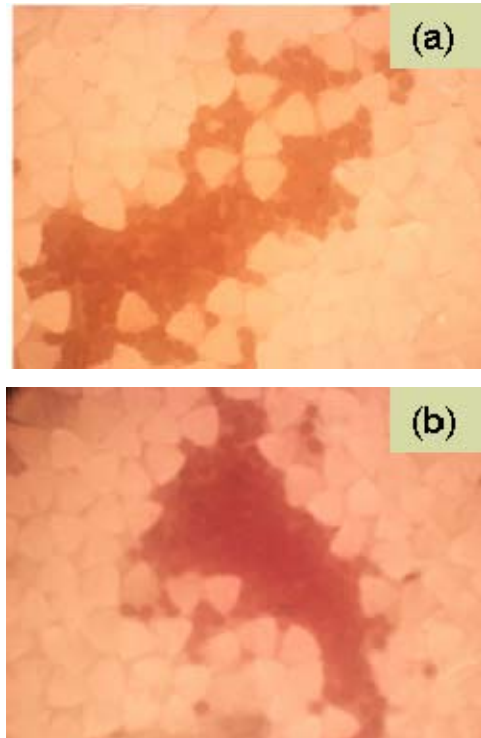


FIGURE 2. Cross-Sections of Loose PP Fiber Bundles Dyed with: (a) C. I. Vat Orange 1; and (b) C. I. Vat Red 1

Dyeing Rate Plots

In order to investigate the compatibility of the identified trichromatic series plus orange dyes, the colorants were combined in equal amounts in common baths, and the optimized batch dyeing process was utilized to generate light, medium and dark shades on the generic PP woven fabric. Absorbance of each dye was recorded at selected times of dyeing (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80 and 90 minutes) at all four wavelengths of maximum absorbance: 515 nm, 540 nm, 665 nm and 475 nm for C. I. Vats Yellow 2, Red 1, Blue 6 and Orange 1, respectively, all converted to their sodium leuco-vat (dianion) forms for absorbance analysis. The exhaustion of each dye was calculated by:

$$\% \text{ Exhaustion} = \frac{(A_o - A_t)}{A_o} \times 100 \quad (4)$$

Here A_o was the absorbance before adding fabric into the dye bath, and A_t was the absorbance at dyeing time t . The dyeing rate plots confirmed the good compatibility of the trichromatic series plus orange colorants in light, medium and dark shades, as reflected by their similar rates of dyeing in combined (and thus competitive) situations (Figures 3-4).

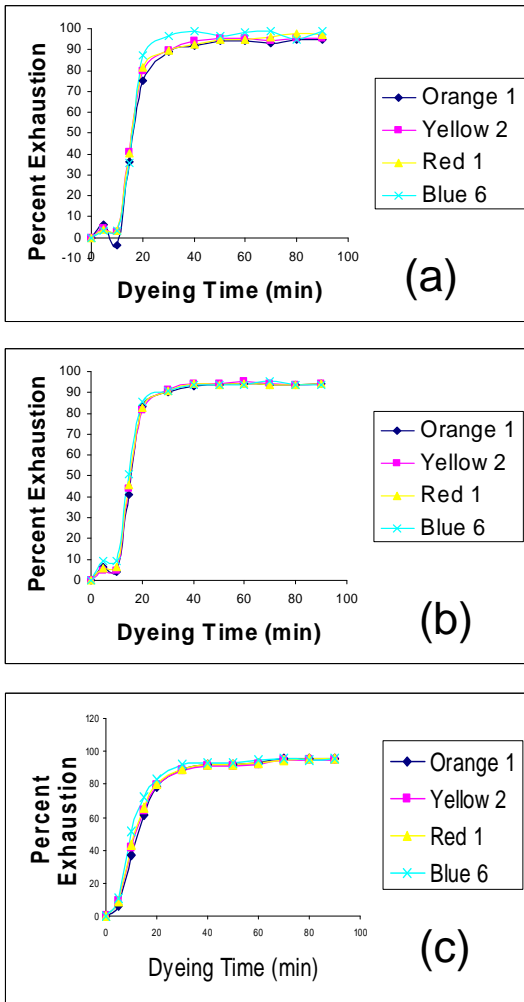


FIGURE 3. Dyeing Rate Plots for the Trichromatic Series plus Orange in: (a) Light Shade; 0.9% owf total dye; (b) Medium Shade: 2.8 % owf total dye; and (c) Dark Shade: 9.4 % owf total dye

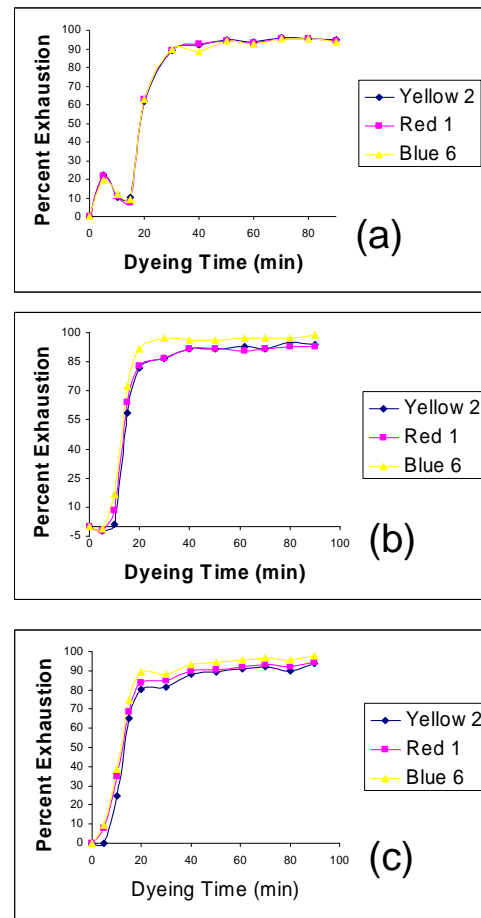


FIGURE 4. Dyeing Rate Plots for the Trichromatic Series in: (a) Light Shade: 0.7% owf total dye; (b) Medium Shade: 2.8 % owf total dye; and (c) Dark Shade: 10.6 % owf total dye

As in the single colorant dyeings, the sorption-desorption instabilities exhibited in the first ~15 minutes were attributed to the rapidly-changing temperature of the bath created by the 2.5°C/minute rate-of-rise employed to reach the 90°C hold temperature (25 minutes required, *Figures 3-4*).

Tensile Testing Results for Dyed and Undyed PP Textiles

Tensile tests of yarns extracted from the dyed and undyed (standard) woven PP fabrics were conducted on an Instron Model No. 5567 frame constant strain rate machine using Bluehill software. A strain rate of 60 mm/min and gauge length of 100 mm was used for all the yarn specimens. Five readings each for warp and weft were taken for all samples and the

average of ten readings was calculated for each sample. The dyed samples did not suffer any significant decrease in load at break, tenacity at break and modulus at break as a result of the optimized, single-stage acid leuco vat dyeing procedure (Figures 5-7).

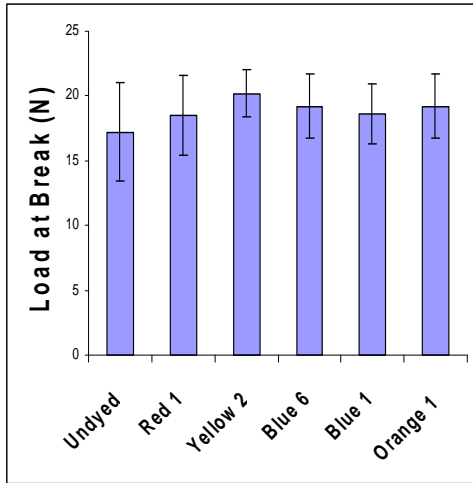


FIGURE 5. Tensile Load at Break for Undyed and Acid Leuco Dyed PP Yarns Extracted From Woven Fabrics

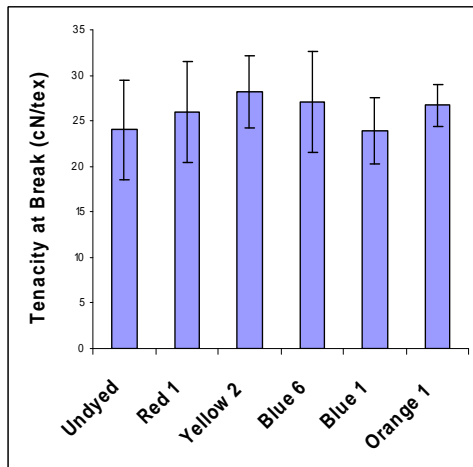


FIGURE 6. Tenacity at Break for Undyed and Acid Leuco Dyed PP Yarns Extracted from Woven Fabrics

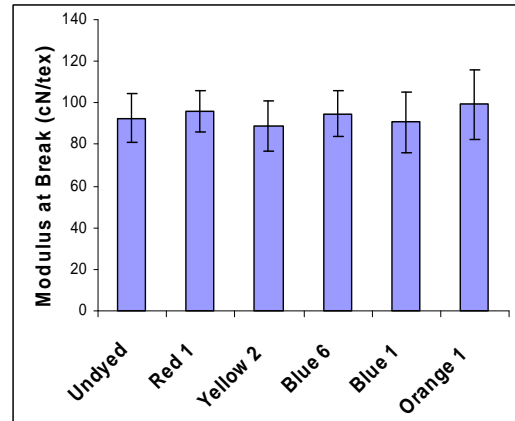


FIGURE 7. Tensile Modulus at Break for Undyed and Acid Leuco Dyed PP Yarns Extracted from Woven Fabrics

K/S Results for Dyed and Undyed PP Textiles

The K/S versus % owf plot detailed that for all the dyes, increasing the amount of colorant in the dyebath resulted in a gradual color buildup on the dyed fabric, followed by saturation (Figure 8). K/S values of the fabrics dyed with the colorants of the trichromatic series plus orange exhibited similar K/S plots (a), whereas those dyed with C. I. Vat Blue 1 alone exhibited higher K/S values (b), reinforcing the compatibility of the component colorants of the trichromatic series plus orange colorants in PP fabric dyeing, along with the incompatibility of Vat Blue 1 with the group. Vat Blue 1 was provided in powder form unlike C.I. Vats: Yellow 2, Orange 1 and Blue 6 which were liquid suspensions. Therefore, true dye content was much higher in Blue 1. Vat Red 1 was also powder but probably had lot of solid dispersing agent added in it. This resulted in Vat Blue 1 dyed fabrics with much higher color strengths than those dyed with the colorants of trichromatic series plus orange.

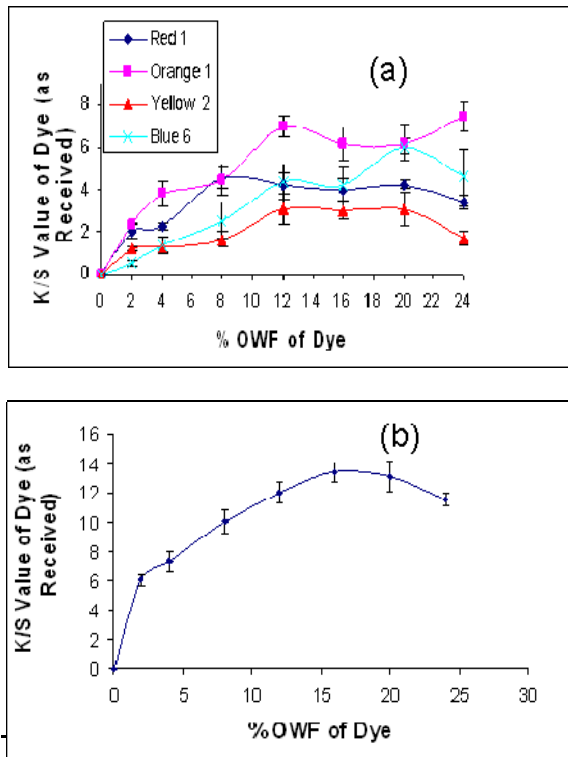


FIGURE 8. K/S Values at Wavelengths of Minimum Reflectance versus % OWF for Acid Leuco Vat Dyed PP Fabrics with, Trichromatic Series plus Orange (a); Vat Blue 1 (b)

X-Ray Diffraction Studies

In order to investigate the effect of the optimized, exhaust batch dyeing process on the solid-state-structure of the PP fiber, Wide-Angle X-ray Diffraction (WAXD) studies were conducted on a Rigaku Micromax-002 WAXS/SAXS system operating at a voltage of 45 kV and a current of 0.66 mA equipped with a Rigaku R-axis IV++ 2-D detection system. The analyses of the diffraction patterns were performed using AreaMax V. 1.00 and MDI Jade 6.1 software. The diffraction patterns (Figure 9), intensity vs. 2θ (Figure 10) and percent crystallinity data (Table I) confirmed the physical testing data that no significant change in the degree of crystallinity of the PP fiber occurred as a result of the optimized exhaust batch dyeing process.

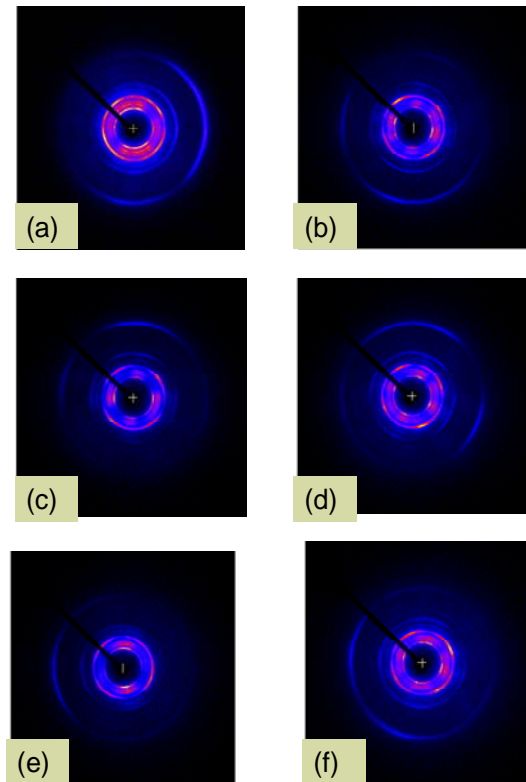


FIGURE 9. Wide Angle X-Ray Diffraction Pattern of PP fabric (a) Undyed; (b) Dyed with Vat Red 1; (c) Dyed with Vat Yellow 2; (d) Dyed with Vat Blue 6; (e) Dyed with Vat Orange 1; (f) Dyed with Vat Blue 1

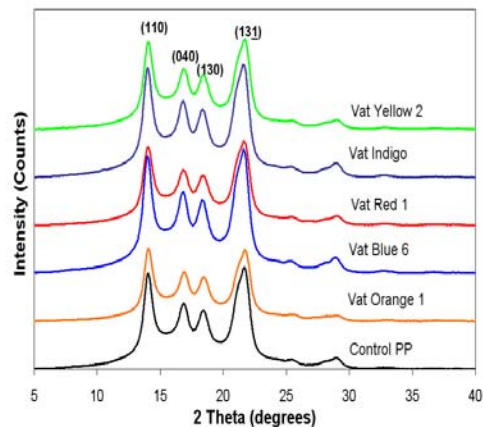


FIGURE 10. Wide Angle X-Ray Diffraction Intensity vs. 2θ Plot for Undyed and Dyed PP Fabrics

TABLE I. Degree of Crystallinity of Control and Dyed PP Fabrics

Name of Dye	Percent Crystallinity
Control	52.9
Vat Red1	48.7
Vat Yellow 2	50.2
Vat Blue 6	53.1
Vat Orange 1	52.9
Vat Blue 1	50.3

Additional Certified Vat Dyes External to the Trichromatic Series

Several additional vat colorants outside the trichromatic series plus orange and indigo group were screened in order to expand the gamut of viable dyes for generic PP coloration via the developed, single-stage, acid leuco batch exhaust process. Several additional vat colorants were demonstrated to have good affinity for the unmodified PP fabric, as evidenced by the CIE L*, a*, b* values obtained from the dyed materials (Table II).

TABLE II. Measured CIE L*, a*, b* Values of Dyed PP Fabrics

C.I. Name of Dye	L*	a*	b*	SPs (cal/cc) ^{1/2}
Orange 15	83.9	4.4	19.0	16.7
Violet 1	55.8	16.0	-14.0	14.8
Green 1	63.6	-21.2	-0.1	14.9
Red 13	70.1	12.2	-2.3	14.8
Yellow 33	79.7	7.9	47.5	16.0

After evaluating wash fastness properties of the dyed fabrics, Green 1 (SP 14.9 (cal/cc)^{1/2}) and Violet 1 (SP 14.8 (cal/cc)^{1/2}) were certified as additional viable colorants for dyeing PP in the developed batch exhaust process. The additional certified vat dyes all had low SP's in their acid leuco forms.

Pad-Steam Dyeing of Unmodified PP Fabric

An unmodified PP fabric was colored with the certified vat dyes using the developed, simulated pad-steam process. The dyed fabrics were measured for K/S values at each dye's respective wavelength of minimum reflectance. Ten measurements were taken for each sample and the average compiled (Table III). C. I. Vat Blue 1 exhibited the highest color strength, while the other dyes also showed good color strength and levelness. In fact, the pad-steam dyed fabrics all exhibited better visual levelness than the corresponding batch dyed fabrics (see the first section under Results and Discussion).

TABLE III. K/S Values Obtained at Wavelength of Minimum Reflectance (8% owf)

C. I. Name of Dye	K/S at Wavelength of Minimum Reflectance
Vat Red 1	2.7
Vat Yellow 2	3.4
Vat Blue 6	3.6
Vat Orange 1	2.1
Vat Blue 1	8.9

Pad-steam dyed fabrics were evaluated for fastness properties by the procedures described in the Experimental Section. The fastness ratings for crocking, washing and dry cleaning are in Tables IV-VI, respectively. The fastness ratings indicated good-to-excellent resistance of the pad-steam dyed PP fabrics to wet/dry crocking, washing and dry cleaning.

TABLE IV. Crock Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Staining Rating	
	Dry	Wet
Vat Red 1	4-5	4-5
Vat Yellow 2	4-5	4-5
Vat Blue 6	4	4-5
Vat Orange 1	4-5	5
Vat Blue 1	4-5	4

TABLE V. Wash Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Red 1	5	5	5	4-5	5	4-5	5
Vat Blue 6	5	5	5	4-5	5	4-5	4-5
Vat Blue 1	5	4-5	4-5	4-5	4-5	5	4-5

TABLE VI. Dry Cleaning Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Red 1	4-5	5	4	4-5	4-5	4-5	4-5
Vat Blue 6	4-5	4-5	4	4-5	4-5	4-5	4-5
Vat Blue 1	4-5	4-5	4-5	4	4	4	4

Pad-Dry Heat Dyeing of Unmodified PP Fabric

An unmodified PP fabric sample (10 gms) was dyed with C. I. Vat Red 1 using the developed, simulated pad-dry heat process. The dyed sample was measured for its reflectance at the wavelength of minimum reflectance and calculated K/S values. Ten measurements were taken for the sample and the average was compiled (*Table VII*).

Table VII. K/S Value Obtained at Wavelength of Minimum Reflectance

Name of Dye	K/S at Wavelength of Minimum Reflectance
Vat Red 1	2.5

The dyed fabric was evaluated for fastness properties by the procedures described in the Experimental Section. The fastness ratings for crocking, washing and dry-cleaning are tabulated in *Tables VIII-X*, respectively. The fastness ratings quantified good-to-excellent resistance of the pad-dry heat dyed PP fabric to crocking, washing and dry-cleaning, respectively.

TABLE VIII. Crock Fastness Ratings of PP Fabric Dyed with C. I. Vat Red 1

C.I. Name of Dye	Staining Rating	
	Dry	Wet
Vat Red 1	4-5	4-5

TABLE IX. Wash Fastness Ratings of PP Fabric Dyed with C. I. Vat Red 1

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Red 1	5	5	5	4-5	4-5	4-5	5

TABLE X. Dry-Cleaning Fastness Ratings of PP Fabric Dyed with C. I. Vat Red 1

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Red 1	4-5	5	4	4-5	4-5	4	4-5

The amount of dye in the exhaust batch process was standardized at 8 % owf. The amount of dye in the

pad-steam and pad-dry heat baths was also taken on the basis of 8% owf and 70% pickup by the PP fabric [11].

Comparison of Various Dyeing Methods

A comprehensive plot was prepared for K/S values of all the fabrics dyed with the certified colorants using the exhaust batch, simulated pad-steam and simulated pad-dry heat methods at their respective wavelengths of minimum reflectance (*Figure 11*).

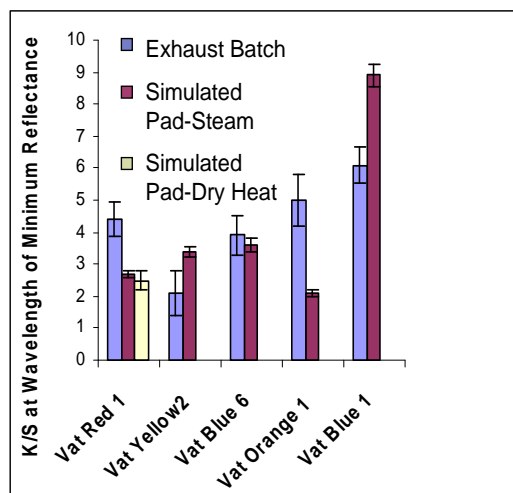


FIGURE 11. Comparison of K/S Values of Vat Dyed PP Fabrics (8 % owf) from Exhaust Batch, Simulated Continuous Pad-Steam and Simulated Continuous Pad-Dry Heat Processes

Using the optimized exhaust batch method as the base, the simulated pad-steam method gave higher fabric K/S values for C. I. Vats Yellow 2 and Blue 1. C. I. Vat Blue 6 gave similar fabric color depth in both the exhaust batch and simulated pad-steam processes. C. I. Vats Orange 1 and Red 1 gave lower fabric K/S values in the pad-steam process than in the exhaust batch process. Further, the fabrics colored by the simulated pad-steam method for all dyes exhibited better levelness than the analogous batch exhaust dyed fabrics, as evidenced by the smaller error bars in *Figure 11*. Similarly, the pad-dry heat process gave a more level C. I. Vat Red 1 dyeing than had been achieved with the exhaust batch process. The simulated pad-dry steam and pad-dry heat processes with C. I. Vat Red 1 gave dyed PP fabrics with similar K/S values.

Gaehr et al. [13] recently reported that Colloisol® vat dyes of BASF (i.e., unreduced, solid pigment particle colorants) gave higher K/S values on pigment-dyed, unmodified PP fabrics after plasma

treatment (K/S values ranging from 2 to 10) as compared to before plasma treatment (K/S values ranging from 1 to 3). The K/S values in *Figure 10* ranged from 2 to 9 for the developed vat dyeing processes, but for most of the certified dyes, the attained K/S values lie approximately in the middle of the values obtained by Gaehr *et al.* for plasma untreated and plasma treated PP fabrics, respectively.

CONCLUSIONS

A viable method to commercially aqueous batch dye generic, unmodified PP fiber textiles in a conventional process has been developed for a certified trichromatic series (red, yellow and blue) plus orange of vat dyes applied in their acid leuco forms, with dyed fabrics exhibiting adequate fastness properties to washing, crocking and dry-cleaning: C. I. Vats Red 1, Yellow 2 and Blue 6 plus Orange 1.

The same method was also shown to adequately color PP textiles with C. I. Vat Blue 1 (indigo) as a stand-alone colorant with adequate fastness properties to washing, crocking and dry-cleaning to produce the popular “denim” shade. The developed single-stage acid leuco method for dyeing generic PP fabrics at pH 7 provided good fastness properties and good color yields without fiber “ring-dyeing.”

Of the vat dyes currently available on the commercial market, C. I. Vat Dyes Red 1, Yellow 2, Blue 1 and Orange 1, all possessing low solubility parameters closest to that of generic PP’s 8.1 (cal/cc)^{1/2}, were demonstrated to be viable candidates for generic PP fiber coloration, while C. I. Vat Blue 6 was deemed a marginal candidate. However, C. I. Vat Blue 6 was the best-performing blue vat dye available outside of C. I. Vat Blue 1, and since the latter was so easily air-oxidized compared to the other candidates for the trichromatic series and was thus incompatible in combination with them, Vat Blue 6 was judged sufficient in performance to move the technology forward into practice.

An exhaustive survey of blue vat dye structures in the Colour Index yielded one colorant that possessed the identified proper solubility parameter and heat of mixing with PP characteristics: C. I. Vat Blue 8. However, the colorant is no longer commercially available on the world market, but with the viable aqueous PP coloration process now developed, vat dye manufacturers should have sufficient incentive to bring C. I. Vat Blue 8 back into production.

Dyeing rate plots with colorant combinations exhibited similar dyeing rate profiles to those of the component dyes. The rate plots confirmed the compatibility of the certified vat dye mixtures (critical for wide shade development of PP products). Cross-sectional microtomes of PP fiber bundles dyed in loose stock form proved complete dye diffusion throughout the fiber structures, i.e., “ring dyeing” was absent in the developed acid leuco vat dyeing process. Tensile testing and X-ray diffraction results quantified the full retention of mechanical and solid-state structure properties of the generic PP fiber after the dyeing process.

Parallel batch exhaust dyeing research certified three additional structures for coloration of generic PP by the single-stage, acid leuco vat dyeing process: C. I. Vats Red 15, Violet 1 and Green 1. All three dyes possessed low SP’s in their acid leuco forms (14.4, 14.8 and 14.9 (cal/cc)^{1/2}), respectively), correlating well with the theoretical and experimental findings of the trichromatic series research.

The developed, simulated pad-steam dyeing method for vat dyeing of generic PP fabric gave higher fabric K/S values than the analogous batch dyed fabrics for C. I. Vats Yellow 2 and Blue 1. C.I. Vat Blue 6-dyed fabrics exhibited similar color depth in both the exhaust batch and simulated pad-steam processes. Fabrics dyed with C. I. Vats Orange 1 and Red 1 by the simulated pad-steam process exhibited lower K/S values than analogous fabrics colored in the exhaust batch process. The simulated pad-steam method for all dyes produced fabrics exhibiting better dye level than analogous fabrics colored by the batch exhaust method, a reflection of the poor bath circulation and pumping pressures of the Roaches Lab Machine through the mounted multi-layered, tightly-woven PP fabrics.

The developed, simulated pad-dry heat dyeing method for C. I. Vat Red 1 on generic PP produced a fabric with a similar K/S value to that generated by the simulated pad-steam method with the same dye at analogous pad bath formulations. Dyed fabrics produced by both the pad-steam and pad-dry heat processes exhibited adequate fastness to wet/dry crocking, washing and dry cleaning.

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