Available online at www.sciencedirect.com
SCIENCE DIRECT
Dyes and Pigments 65 (2005) 137–143
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Indigo adsorption properties to polyester fibers of different levels of fineness

Young-A. Son[a,*], Hyeong-Tae Lim[a], Jin-Pyo Hong[a], Tae-Kyung Kim[b]

[a]*Department of Textile Engineering, Chungnam National University, Daejeon, 305-764, South Korea*
[b]*Korea Dyeing Technology Center, Daegu, 703-834, South Korea*

Received 2 March 2004; received in revised form 14 May 2004; accepted 15 July 2004
Available online 17 September 2004

Abstract

The dyeing behaviors using indigo vat dye on conventional and microfiber polyester and its fastness properties to washing were examined. Acid leuco dyeing technique with acetic, formic and citric acids was considered. The effect of urea addition to improve the dye build-up was also investigated. In addition, repeated multiple washings of indigo dyeings, which were compared to the results of disperse dyeings, were carried out to determine the fastness properties. From the obtained results, it is found that acid leuco form provided a satisfactory dye uptake at different pH ranges and that the improved dye build-up characteristic was achieved by urea addition due to increasing dye solubility and dye penetration within the substrates. The fastness to washing of indigo dyeings was more effective than that of comparable depth of disperse dyeings.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: Indigo; Polyester; Microfiber; Wash fastness; Acid leuco; Urea; Disperse dyes

1. Introduction

In a previous research [1], fundamental dyeing behaviors of indigo on polyester fibers were examined. Because most dyeing application using vat dyes was confined to the cellulosic fibers, little attention has been paid to the application of vat dyes on synthetic fibers [2–7]. There is little satisfactory blue azoic combination for use on polyester, but attractive color of indigo vat dyes may be used to provide the desired shade where the dyed materials are required to have exceptionally good fastness properties, particularly to repeated washing.

It was found that even though a ring dyeing of fiber surface is expected from vat dye application, resulting indigo dyeing on to polyester substrates at 120 °C clearly showed the complete penetration of indigo molecules into the interior area of the substrates in full [1]. The cross-sectional photographic evidence of dyed fibers has also verified the complete dye exhaustions. Besides, it was proposed that as indigo dyeing proceeded, two new components were converted from original indigo molecules and the corresponding structural changes were attributed to the reduction in color strength of dyed samples. In the case of dyeing methods, it was revealed that simple dispersion method of indigo had little influence on increasing the dye exhaustions whereas the leuco form method was able to impart a satisfactory color yield to the polyester fibers.

To examine the indigo adsorption properties to polyester fibers of different levels of fineness, this work herein concerns an investigation of the dyeing behaviors on conventional and microfiber polyester and the fastness properties to washing. In order to improve the build-up characteristic of indigo on to the both conventional and microfiber substrates, acid leuco

* Corresponding author. Tel.: +82 42 821 6620; fax: +82 42 823 3736.
E-mail address: yason@cnu.ac.kr (Y.-A. Son).

0143-7208/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2004.07.008

technique prepared by using acetic, formic and citric acids was considered. The effect of urea addition to enhance dye exhaustions was also investigated. In addition, repeated multiple washings of indigo dyeings for conventional and micro-fineness polyester fibers were carried out to determine the fastness properties.

2. Experimental

2.1. Materials

Conventional polyester fabric (75f36, 2 denier/filament) and microfiber polyester (75f24f40, 0.08 denier/filament) were used in this experiment. Indigo employed in this work was purchased from Aldrich Chemical Company. Thiourea dioxide as a reducing agent was purchased from Aldrich Chemical Company. For reduction clearing, a commercial sample of non-ionic surfactant *Sandopur MCL Liq*. was generally supplied by Clariant. All other chemicals used were laboratory grade reagents.

2.2. Dyeing

Both conventional and microfiber polyester were dyed in sealed, stainless steel dye pots of 120 cm^3 capacity in a laboratory-scale dyeing machine (ACE-6000T). Samples were placed in a 40 °C dyebath of 20:1. After 10 min, the temperature was raised until reaching 70 °C. At this temperature, the vatting of indigo was sustained for 30 min. At the end of vatting, polyester samples were added into the bath and temperature was then increased to the range of 90 °C–130 °C. At the end of dyeing, the dyed samples were removed, rinsed thoroughly in tap water and allowed to oxidize in the open air.

2.3. Reduction clearing

After oxidation, the samples were reduction cleared to remove the loosely fixed dye on the surface of dyed fibers. The dyed samples were washed off using 1 g/l of $Na_2S_2O_4$, 2 g/l of Na_2CO_3 and 2 g/l of a non-ionic surfactant at 60 °C for 20 min and were then rinsed in running tap water.

2.4. Acid leuco moiety

The vatting of indigo commenced at 40 °C, with the addition of 2 g/l of Na_2CO_3 and 5 g/l of thiourea dioxide. After raising the temperature to 70 °C, vatting was continued for 30 min. With the completion of vatting confirmed by the color change of the bath solution (lemon-yellow), the non-ionic dispersing agent with constant stirring was added to the solution and an addition of acetic acid, formic acid and citric acid was then followed to bring proper acid pH ranges. This process produced the acid leuco moiety of indigo at each pH condition and provided a stable dispersion of acid leuco moiety.

2.5. Urea addition

To increase dye solubility and fiber swelling, an addition of urea was considered to improve dye build-up characteristic. Urea (10 g/l) was added to the bath at each dyeing temperature.

2.6. Color measurement

Colorimetric data of indigo dyeings were determined using a *Datacolor SF 600 plus* spectrophotometer interfaced to a PC. Measurements were taken with the specular component of the light excluded and the UV component included, using illuminant D_{65} and 10^o standard observer. Each fabric was folded once so as to give two thickness and average of five readings was taken each time.

2.7. Preparation of comparable disperse dyeing

The disperse dyeings of conventional and microfiber polyester having a similar color strength with indigo

Table 1
Colorimetric data for indigo dyeings at various temperatures

	Temp. (°C)	L^*	a^*	b^*	C	h°
Conventional fiber type	90	57.64	−7.85	−19.20	20.74	247.77
	100	43.18	−7.47	−22.75	23.95	251.83
	110	29.81	−1.59	−20.62	20.69	265.59
	120	24.78	0.70	12.40	12.45	273.22
	130	26.71	0.67	−10.40	10.42	273.71
Microfiber type	90	48.27	−10.06	−21.95	24.15	245.38
	100	41.52	−10.39	−24.49	26.60	247.01
	110	42.87	−9.46	−23.92	25.72	248.41
	120	45.58	−8.49	−22.10	23.67	248.99
	130	40.05	−4.95	−20.22	20.81	256.23

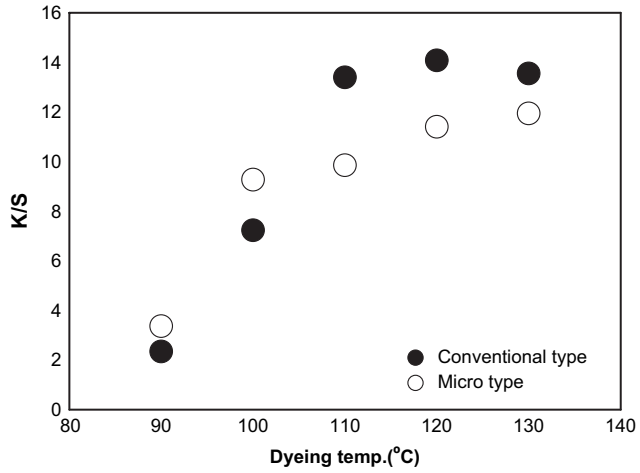


Fig. 1. Effect of dyeing temperatures on color strength of indigo dyeings.

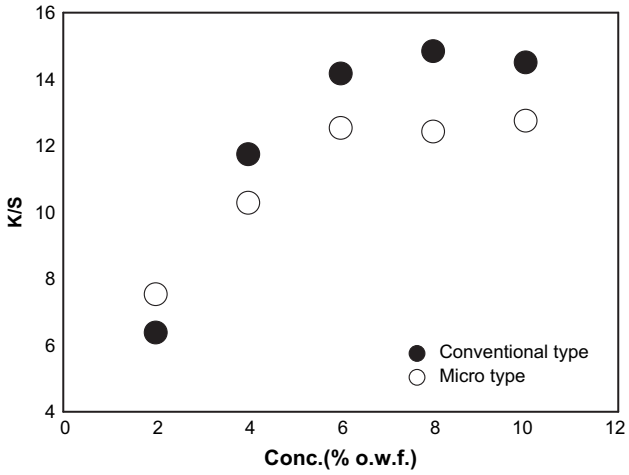


Fig. 2. Effect of dye concentrations on color strength of dyeings.

dyeings were prepared using color matching system (*Datacolor SF 600 plus*) to compare the wash fastness properties. This disperse dyeing was prepared with the following chosen dyes: C.I. Disperse Yellow 54, C.I. Disperse Red 167 and C.I. Disperse Blue 79.

2.8. Wash fastness test

The wash fastness of the dyeings was tested using the method of ISO 105 C06 A1S [8]. SDC multifiber strip fabric as an adjacent material was used. The samples were sequentially washed five times.

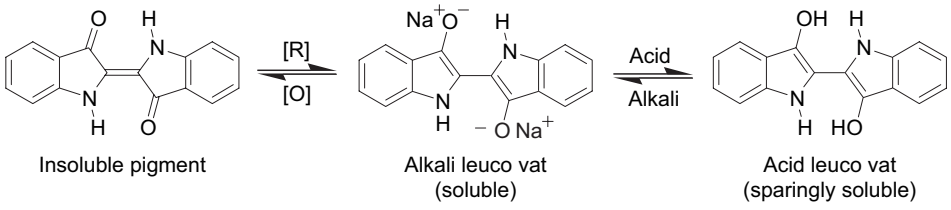
3. Results and discussion

3.1. Dyeing properties

In order to investigate the adsorption properties, both conventional and microfiber polyester were dyed with indigo at various temperatures (90–130 °C). Thiourea dioxide (2 g/l) as a reducing agent, 5 g/l of Na_2CO_3 and 6% owf of indigo were applied. Table 1 and Fig. 1 show the colorimetric data and the color strength of indigo dyeings on both conventional and microfiber substrates.

These data show that the color strength of the indigo adsorption increased with increasing application temperature. Clearly, the dye adsorption was more favorable at higher temperature than at lower temperature.

At higher temperature, this observation could be attributed to the corresponding diffusional power within the higher crystalline structure of polyester molecules. Also the higher kinetic energy of the indigo molecules and the higher swelling effect of the substrates resulted in the increased color strength. In this context, it is thought that in terms of dyeing temperature, even though the vat dyes are commonly applied to the cellulosic fibers around 60 °C, the adsorption behaviors of indigo on both polyester fibers with different levels of fineness are following a similar dyeing manner for commercial disperse dyes, which involved high-pressure and high-temperature conditions. In the case of micro-type polyester fibers, the levels of color strength at maximum dye exhaustion were lower than those of conventional fineness substrates. Microfiber has a greater fiber surface area than conventional counterpart. As the diameter of the individual fiber become smaller, the total surface of the fiber or textile fabric increases exponentially. Thus, the reason of low color strength for dyeings on to microfiber polyester is the greater reflection of light from the fiber surface. In this context, the greater surface area per unit mass of microfiber could create



Scheme 1. Application of indigo vat dye.

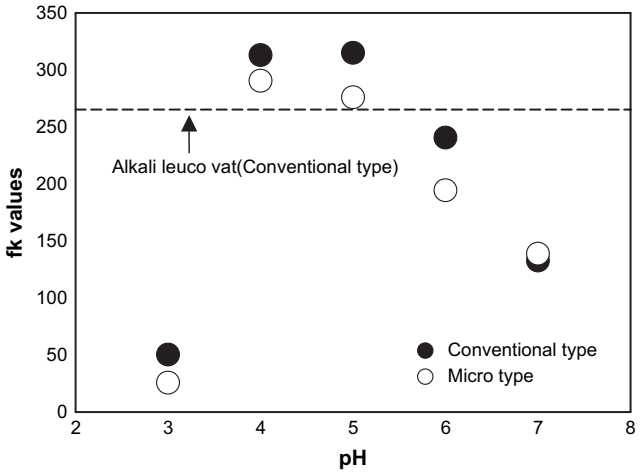


Fig. 3. Effect of acid leuco dyeing using formic acid.

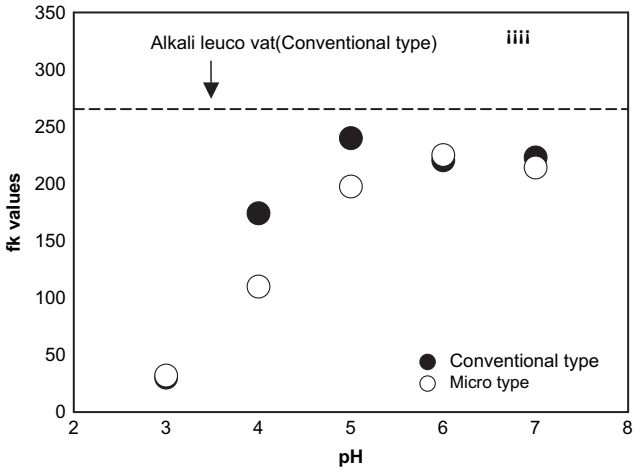


Fig. 5. Effect of acid leuco dyeing using citric acid.

problems in terms of fastness to washings. The requirement of a higher amount of dye due to greater fiber surface area results in low wet fastness properties of dyeings on microfiber. The wet fastness properties will be discussed in the following section.

In Fig. 2, the dyeing properties of indigo using different dye amounts were examined. The color strength of the both dyed samples reached saturation values around the dye amount of 6% owf. Also Fig. 2 reveals that the lower dye uptake was observed from the microfiber side. As described earlier, the greater surface area is attributed to the corresponding lower color strength caused by reflection of light from the fiber surface.

The use of indigo vat dye is commonly confined to cellulosic fiber on which they exhibit excellent light and wet fastness properties. This cellulosic fiber shows hydrophilic characteristic of the substrate which imparts substantivity to the anionic dyes. Reduced indigo, namely alkali leuco moiety, exhibits hydrophilic properties capable of attraction on to cellulosic fibers. However, in the case of hydrophobic fiber, more hydrophobic dye moiety such as acid leuco form may be suitable for higher dye exhaustion. In this context, to improve dye build-up a sparingly soluble acid leuco form can be considered for dyeing approach to the hydrophobic substrates. As well known, indigo dye contains two conjugated carbonyl groups which are converted by reduction under alkaline conditions [3,4]. When acid is added, the alkali leuco form is converted into the sparingly water soluble acid leuco moiety which can be used in the dyeing of hydrophobic substrates-Scheme 1.

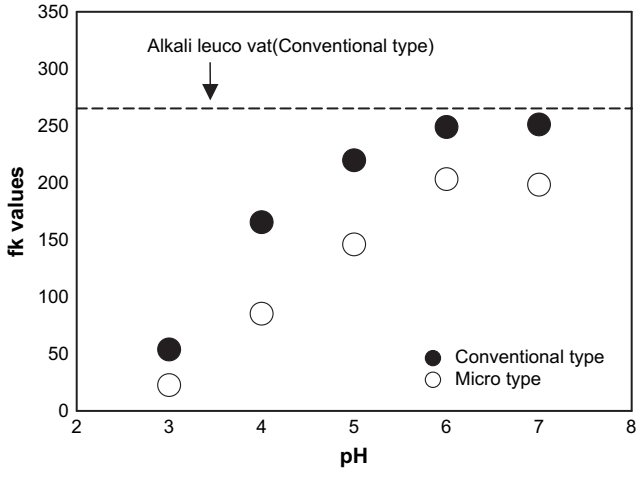


Fig. 4. Effect of acid leuco dyeing using acetic acid.

This sparingly soluble vat acid derivative behaves as disperse dyes in terms of its exhaustion characteristic. When oxidized back to the insoluble vat pigment form within the substrate, it provides excellent wet fastness properties.

Total color yields (fk values) of the indigo dyeings obtained by the acid leuco form are shown in Figs. 3–5. As expected the dispersion of the acid leuco moiety of indigo behaved as a disperse dye and dyed both the polyester substrates in a satisfactory manner.

The corresponding results showed different dye build-up behaviors with each applied acid type. In the case of acid leuco dyeing using formic acid, it shows high

Table 2
Methods used to retard oxidation on the surface of fibers

Rinse condition (60 °C, 60 min)	L^*	a^*	b^*	C	h°	K/S
Nil	33.24	−4.51	−17.89	18.45	255.86	11.19
2 g/l Na_2CO_3	34.89	−4.51	−22.53	22.97	258.67	11.16
1 g/l sodium dithionite	37.12	−6.45	−17.02	18.2	249.23	9.44
2 g/l Na_2CO_3, 1 g/l sodium dithionite	36.59	−6.64	−16.13	17.44	247.63	9.42

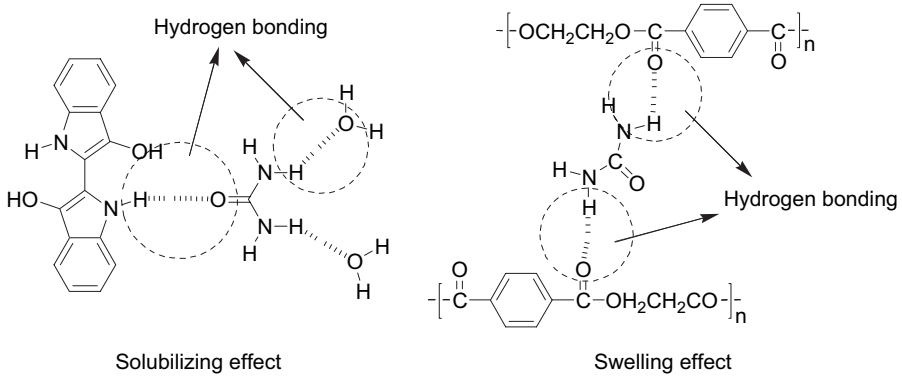


Fig. 6. Effects of urea addition for indigo dyeings on polyester substrates.

adsorption characteristic at the range of pH 4–5, where the fk value was higher than that of alkali leuco dyeing. Other acid leuco dyeings using acetic acid and citric acid exhibit that higher color strengths of the dyeing were obtained at the range of pH 5–6 and pH 6–7, respectively. Also, these two types showed similar color values compared to that of alkali leuco dyeing. No exact explanation can at present be offered to explain the dye uptake variations occurred due to acid types. Further investigations are needed to explain these findings. The dyeing application using acid leuco form on to hydrophobic substrates is a considerable alternative to increase dyeing uptakes. Particularly, the acid leuco moiety using formic acid exhibited greater color strength values.

In order to inhibit rapid dye oxidation on the fiber surface, the dyed samples were rinsed prior to oxidation so as to retard rapid dye oxidation on the surface of substrates as such loosely fixed dye could result in evident poor fastness. As shown in Table 2, the color strength of rinsed samples compared to nil sample slightly decreased, which may represent the retardation of dye oxidation on the fiber surface. Even though higher levels of wet fastness are still left to be achieved using reduction clearing process, these rinsing methods could be appreciable.

3.2. Effect of urea addition

Having ascertained that indigo dyeings on both conventional and microfiber polyester were satisfactorily achieved, a further set of experiments to enhance dye build-up was examined in terms of the effect of urea addition. It is expected that by adding urea to the bath, better color value, better penetration and improved fastness could be achieved. This urea addition can impart better solubilizing effect to indigo molecules and higher swelling effect to substrates (Fig. 6). Thus, the increased dye build-up could be obtained by this attempt due to greater ease of access of indigo molecules to all parts of the swollen polyester substrates.

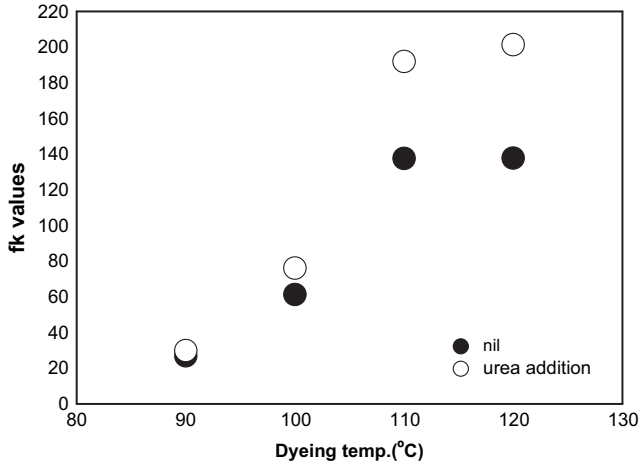


Fig. 7. Effect of urea addition on conventional fiber type at various temperatures.

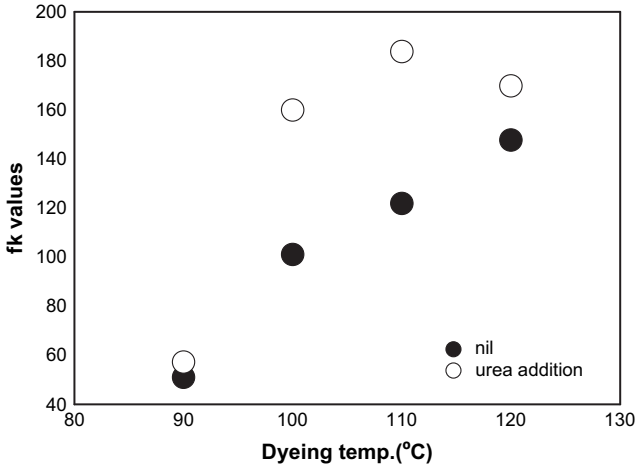


Fig. 8. Effect of urea addition on microfiber type at various temperatures.

Table 3
Colorimetric data of dyeings with indigo and disperse dyes on the conventional and microfiber types [1]

	Dyes	L^*	a^*	b^*	C	h°	fk
Conventional fiber type	Indigo dyeing	26.44	5.03	−13.73	14.63	290.13	237.15
	Disperse dyeing	26.23	2.86	−14.47	14.75	281.20	236.75
Microfiber type	Indigo dyeing	30.29	−1.04	−23.73	23.75	267.49	207.73
	Disperse dyeing	30.37	−2.54	−23.65	23.78	263.87	204.06

Figs. 7 and 8 show the effects of urea addition on the color strength of the both conventional and microfiber polyester at various dyeing temperatures. It is found that the color strength of both the polyester substrates obtained in the presence of urea was higher than that of non-added samples. This observation that the extent of adsorption of indigo on to conventional and microfiber polyester increased with urea addition was attributable to the increased indigo solubility, together with the increased fiber swelling that accompanied a temperature increase in the presence of urea.

3.3. Wash fastness

The wash fastness test of both the conventional and microfiber dyeings with indigo and disperse dyes, showing a similar color depth of shade, was carried out. The disperse dyeing having the same color strength with indigo was prepared using color matching system.

Table 3 displays the colorimetric data of both conventional and microfiber dyeings with indigo and disperse dyes. It is evident that when compared to the colorimetric data of both indigo samples, virtually similar color strengths (fk values) were obtained by the dyeings of disperse dyes. In this context, it is suggested that these disperse dyeing specimens of conventional and microfiber are quite appropriate for the comparison of wash fastness. From Tables 4 and 5, the corresponding assessments show that the indigo dyeing displayed very good fastness properties to the five multiple washes in terms of shade change and that very little staining to the adjacent multifiber strip occurred. This satisfactory result can be attributed to the insoluble characteristic of indigo molecules. Clearly, the dyeing prepared by indigo was more effective in the reduction of dye loss than that of disperse dyeing.

4. Conclusions

In this work, the dyeing behaviors and wash fastness properties using indigo vat dye were examined. Both conventional and micro-fineness polyester were used in this study. The color strength of indigo dyeings on to both polyester substrates generally increased with increasing application temperatures. This adsorption behavior at higher temperature could be attributable to the greater diffusional power of indigo molecules within the substrates and the higher fiber swelling effect. As expected, the dispersion of the acid leuco moiety of indigo behaved as disperse dyes and dyed both the polyester substrates in a satisfactory manner. Particularly, the acid leuco moiety using formic acid exhibited greater color strength values. The enhanced dye build-up was obtained by urea addition due to higher dye solubility and greater ease of access of indigo molecules to all parts of the swollen polyester substrates. For both conventional and microfiber polyester, the wash fastness properties of indigo dyeings were more effective than those of comparable depth of disperse dyeings.

Table 4
Grey scale assessments for indigo and disperse dyeing on conventional type [1]

	Washes	Change in color	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Indigo dyeing	1	–	5	5	4–5	5	5	5
	2	–	5	5	4–5	5	5	5
	3	–	5	5	4–5	5	5	5
	4	–	5	5	5	5	5	5
	5	4–5	5	5	5	5	5	5
Disperse dyeing	1	–	3–4	4–5	3–4	3–4	4–5	4
	2	–	4	4–5	4	4	4–5	4–5
	3	–	4–5	5	4	4	5	4–5
	4	–	4–5	5	4	4	5	4–5
	5	4–5	5	5	5	5	5	5

Table 5
Grey scale assessments for indigo and disperse dyeing on microfiber type

	Washes	Change in color	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Indigo dyeing	1	–	4	4–5	4	5	5	5
	2	–	4–5	4–5	4	5	5	5
	3	–	4–5	4–5	4	5	5	5
	4	–	5	5	4–5	5	5	5
	5	4	5	5	4–5	5	5	5
Disperse dyeing	1	–	3–4	4–5	3–4	3	4–5	4
	2	–	4	4–5	3–4	3–4	4–5	4–5
	3	–	4	5	4	4	5	4–5
	4	–	4–5	5	4	4	5	4–5
	5	4	5	5	5	5	5	5

Acknowledgments

This work was supported by grant no. R05-2002-000-01033-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

References

[1] Son Y, Hong J, Kim T. Dyes Pigments 2004;61:263–72.
[2] Campbell B. J Soc Dyers Colour 1966;82:303–13.
[3] Hunger K. Industrial dyes: chemistry, properties, applications. Wiley-VCH Publishing Company; 2002.
[4] Preston C. The dyeing of cellulosic fibres. West Yorkshire: The Dyers Company Publications Trust; 1986.
[5] Kang J, Ryu H. J Korean Soc Dyers Finishers 2001;13:241–8.
[6] Jang H, Kim H, Lee M. J Korean Soc Dyers Finishers 2001;13:329–35.
[7] Aspland J. Text Chem Color 1992;24:27–31.
[8] Anon. Methods of test for colour fastness of textiles and leather. 5th ed. Bradford: Society of Dyers and Colourists; 1990.