Al-Azhar Bull. Sci. Vol. 17, No. 1 (June.): pp. 127-138, 2006

NEW APPROACHES FOR DYEING POLYESTER WITH INDIGO DYES

NAGIA F. ALI, and S. SHAKRA

Textile Research Division. National Research Center, Dokki, Cairo Egypt

Abstract

Polyester fabric was successfully dyed with indigo dyes using Iron(II) salt complex and dextrose as a substitute for sodium hydrosulphite. The dyeing efficiency of these systems were compared with those of the conventional system using sodium hydrosulphite. Results of the color strength of the obtained dyeings are higher than those for hydrosulphite. Furthermore, dyeings obtained with the new reducing systems exhibit very good fastness properties. Rubbing fastness on polyester dyed with indigo is superior to that on cotton.

Keywords: Dyeing, Hydrosulphite, Iron complexes, Dextrose, Reduction, Indigo dyes, polyester.

Introduction

Indigo was the most important of the natural dyes in ancient times and has retained its importance up to the present day. A variety of plants including woad, have providing indigo but most natural indigo is obtained from those in the genus *Indigoferea*. From practical indigo dyed clothes such as aizome to modern fashionable jeans, indigo has always had a wide field of application[1,2]. Morever, the chronic and acute toxicity of indigo is very low [3]. Indigo, which is a vat dye, has an affinity for cotton, wool and silk fabrics in its leuco form [4], but it has a low affinity for synthetic fabrics such as polyester.

Several investigators attempted to dye polyester fabrics with indigo to seek a part of the large market share [5,6]. Chevli and Lewis proposed a leuco vat acid method in which organic acids such as citric acid were added to bring the pH below 7 [6]. However, this method required additions of organic acids, which increased the cost of treating a huge amount of wastewater. Sodium hydrosulphite is universally recognized as the most appropriate reducing agent for reduction of vat dyes during dyeing of cotton based textiles. It is as well to emphasize that sodium hydrosulphite cannot be recycled and the disposal of dyeing baths and rinsing water causes high costs and various problems with the effluent (high salt load, depletion of dissolved oxygen, problems with *nasal nuisance*, toxicity of sulphide, etc.). This means that modern economical and ecological requirements are not fulfilled [7,8 and 9].

Alternative eco-friendly reducing systems including hydroxyl acetone, glucose-NaOH, and electrochemical reduction were reported (10-13). Ferrous hydroxide, Fe $(OH)_2$, though a strong reducing agent, is ineffective in aqueous systems due to poor water solubility. To exploit the reductive potential of Fe $(OH)_2$ by increasing its water solubility, coordination complexes of Fe (II) salts with suitable ligands can be prepared in the presence of alkali, such as NaOH. Fe (II)-gluconic acid complexes have been reported (8, 15) to have sufficient water solubility for vat dye reduction and subsequent dyeing of cotton at 60°C. This Fe (II) reduction bath was turbid due to incomplete solublization of Fe $(OH)_2$; although effective for the reduction of indigo (15). Dextrose is also a strong and eco-friendly reducing agent for vat dyes.

In this paper, we demonstrate the possibility of dyeing polyester fabrics with indigo and indigo carmine (fig. 1&2) by using

1- Iron (II) salt consists of $FeSO_4$ and gluconic acid.
2- Dextrose – NaOH.
3- High temperature dyeing as disperse dye, and comparing these methods with the hydro method by controlling the ratio of sodium hydrosulphite and sodium hydroxide concentration in the dyebath solution at a mild temperature. We also compare dyeing performance for color for the polyester and cotton fabrics using a reflection spectroscopic analysis.

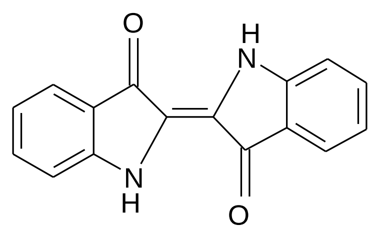

Figure 1. Structure of indigo (oxidized form)

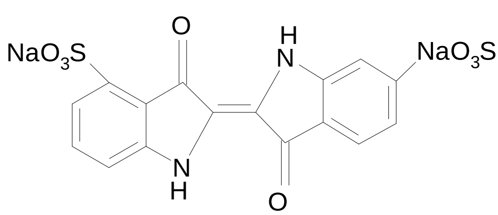

Figure 2. Structure of indigo carmine (oxidized form)

Experimental

Materials

Fabrics

Polyester (70 g/m2, number of threads in the warp 210/5cm and in the weft 191/5cm, warp 8.3 tex) and mill-scoured and bleached Cotton fabric (140 g/m2) was supplied from Misr Co. for Spinning and Weaving, El-Mehalla El- Kubra, Egypt. The fabric was treated with 5 g/l. sodium carbonate along with a wetting agent (Hostapal. Hoechst Co.), at the boil for 4 hours. The fabric was then thoroughly washed with water and dried at ambient temperature.

Dyes

Commercial indigo blue grain dye. Lot 2500203 (Singochem Ningbo), and indigo carmine (C.I. No. 73015) were used without further purification.

Dyeing procedure of polyester and cotton with the hydro bath

Indigo dye was reduced in aqueous solutions of 3-10 g/l sodium hydrosulfite ($Na_2S_2O_4$) and 0.5-2.5 g/l sodium hydroxide at 80, 100, and 120^{o}C for 30 minutes. The bath ratio was 40:1 and the dye concentration was 0.05-3% owf. The typical dyeing procedure for polyester was 8g/l sodium hydrosulfite, 0.5 g/l NaOH and 1% owf dye at 120-130 ^{o}C. Polyester fabric was dyed in sealed, stainless steel dye pots in dyeing machine. Samples were placed in 40^{o}C dyebath of 40:1. After 10 min, the temperature was raised until reaching 70^{o}C. At this temperature the vatting of indigo was continued for 30 min. With completion of vatting confirmed by the color change of the bath solution, the non-ionic dispersing agent with constant stirring was added to the solution and an addition of acitic acid was given to bring acid pH conditions, which produced the acid leuco form of indigo and provided a stable dispersion of acid leuco dye. At the end of vatting, a polyester sample was added and temperature was then increased to the range of temperatures of 90-130^{o}C. At the end of dyeing, the dyed samples were removed, rinsed thoroughly in tap water and allowed to oxidize in the open air.

Dyeing polyester and cotton with the Iron (II) salt bath

In the Iron (II) salt method, gluconic acid (5.6 ml, 50%), was dissolved in 100 ml of water in a glass beaker open to air and, ferrous sulfate ($FeSO_4$, 2g) was dissolved in this bath ($FeSO_4$: ligand molar ratio = 1:2) followed by the addition of caustic soda (NaOH), 1.21 g, the bath was turbid. The quantity of dye required to get 1%

owg depth of shade was then added. Vatting and dyeing was carried out at 60°C. dyeing polyester was carried out at 120-130^{o}C as the previous technique.

Dyeing polyester and cotton with dextrose

About 150ml of 0.1 M dextrose was poured into a bottle. 6ml of 3M NaOH solution was added, the quantity of dye required to get 1% shade was then added . Vatting and dyeing was carried out at 60^{o}C. dyeing polyester was carried out at 120-130^{o}C as the previous technique.

Dyeing polyester under pressure

Dyeing of polyester samples was carried out at a temperature of 130^{o}C for 45 minutes under pressure in cooking bottle in the presence of dispersing agent (sodium lignin sulphonate) (1:1) ratio of the dye weight and a few drops of acetic acid (pH 5), after dyeing the samples thoroughly washed and then subjected to a surface reduction clearing.

Surface reduction clearing of dyeing

At the end of dyeing, the samples were reduction cleared to remove the loosely fixed dye on the surface of dyed fibbers. A surface reduction cleaning solution consists of 5g/l NaOH + 6g/l sodium hydrosulfite. The sample was heated in this solution for 10 minutes, at 60^{o}C. The sample was thoroughly washed and then air dried.

Color Strength

The reflectance of the soaped samples was measured on a Perkin – Elmer Lambda 3B UV/vis spectrophotometer. Relative color strengths (K/S value) were determined using the kubelka- Munk equation [14].

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

Where R = Decimal fraction of the reflactance of dyed fabric.
R_o= Decimal fraction of the reflactance of undyed fabric.
K = Absorption coefficient, and
S = Scattering coefficient.

Fastness testing

The dyed samples were tested according to ISO standard methods [15]. The specific tests were: ISO/105 X12 (1987), color fastness to rubbing, ISO 105; ISO

105- C02 (1989), color fastness to washing, ISO 105-E04 (1989, and ISO 105 – B02 (1989); color fastness to light (carbon arc)

Results and Discussion

The effect of sodium hydrosulfite concentration on dyeing polyester fabric with indigo dyes under investigation in a dyebath solution containing sodium hydrosulfite and sodium hydroxide at 120^{o}C for 30 minutes is shown in figure 3. At a constant concentration of 1g/l sodium hydroxide, the total K/S value increased with an increasing concentration of sodium hydrosulfite. This increase is almost saturated over the concentration of 8g/l.

The effect of sodium hydroxide concentration on dyeing polyester fabric with indigo and indigo carmine is shown in figure 4. The K/S value decreased with increasing concentration of sodium hydroxide over a range of 0.5g/l. The effect of the sodium hydroxide concentration was not enough at 0.2 g/l sodium hydroxide. Proper concentrations of sodium hydrosulfite and sodium hydroxide were important for indigo dyeing of polyester fabrics. This phenomena are explained by the molecular structure and reduced form of indigo(16) .

The typical forms of reduced indigo dye are illustrated in figure 5. Sodium hydrosulfite can reduce indigo and produce the three different forms of reduced indigo by carefully controlling the dyebath pH (16). In presence of sodium hydroxide, the di-sodium arylenolate form (Figure 5a, di-ionic form) and the mono-sodium arylenolate form (figure 5b, mono ionic form),which are water-soluble, are formed in the dyebath. The nonsodium arylenolate form (Figure 5c, non-ionic form) is formed at low pH dyebath. The ionic forms, which are more hydrophilic than the non-ionic form, have a high affinity for cellulose fabrics such as cotton (17). However, the ionic forms have a low affinity for polyester fabrics, which are more hydrophobic than cellulose fabric (18). The hydrophilic cotton fabrics could be dyed with indigo dissolved in an aqueous solution including a small amount of sodium hydrosulfite and sodium hydroxide. The polyester fabrics could not be dyed well with the ionic forms under the same conditions as shown in table 1. When the smaller amount of sodium hydroxide was added, the pH value, which was measured after dyeing, was in the neutral to acid range using sodium hydrosulfite (8g/l) and sodium hydroxide (0.5 g/L) decreased the amount of ionic forms and increased the amount of the non-ionic form which has a higher affinity for polyester fabrics than the ionic forms (18).

Table 1. Influence of dyeability of polyester fabric samples with indigo dyes using different NaOH concentrations on pH values (Indigo 1% owf, bath ratio, 40:1, dyeing time. 30 minutes, at 120oC).

$Na_2S_2O_4$, g/l	NaOH, g/l	pH	K/S	Forms of reduced indigo
3	0.2	5	15.7	non-ionic
3	1	7	18.2	non-ionic
3	2.5	11	1.2	ionic

Effect of dye bath temperaturer

The effect of the dyebath temperature on indigo dyeing of polyester fabric is shown in figure 6. The K/S value increased with increased dyeing temperature. We considered that at a higher temperature, the solubility of the indigo dye in the aqueous solution increased, and the amorphous regions of the polyester fabrics expanded, so the polyesters were dyed with indigo. Dye molecules cannot penetrate the highly ordered crystalline regions of polyester, their adsorption can only take place in the amorphous regions, which are not highly ordered (18). Because of the extension in the amorphous region of polyester, a high temperature over 100oC is a must.

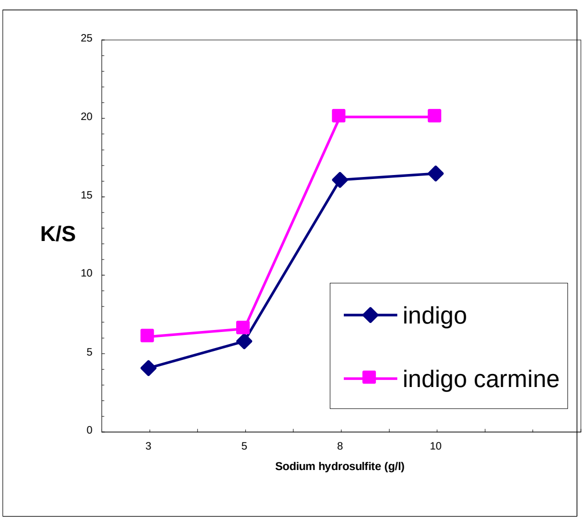

Figure 3: Effect of $Na_2S_2O_4$,concentration on dyeing polyester fabric, 1% owf dye, 40:1 bath ratio, at 120°C for 30min.

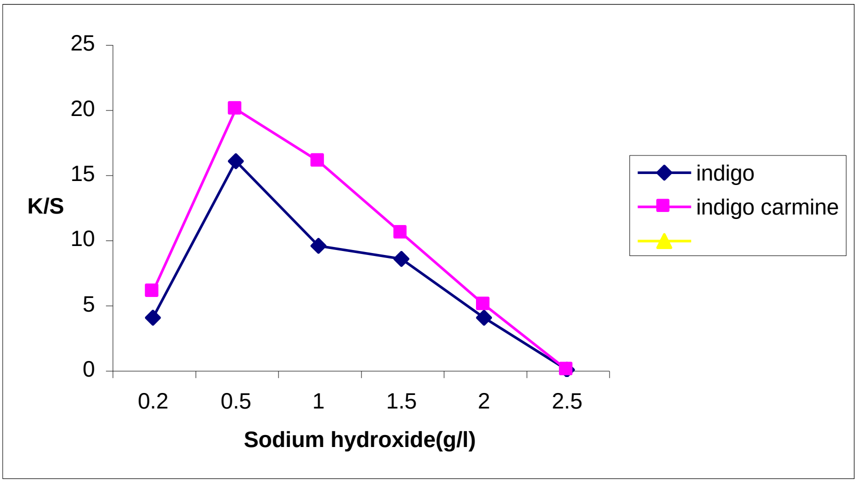

Figure 4: Effect of (NaOH) concentration on dyeing polyester fabric, 8g/l $Na_2S_2O_4$, 1% owf dye, 40:1 bath ratio, at 120^{o}Cfor 30min.

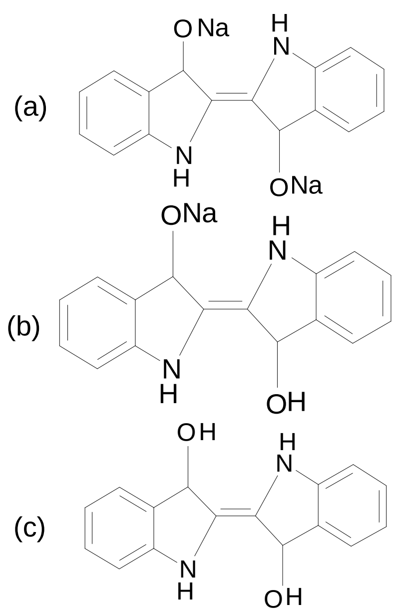

Figure 5. Structure of reduced indigo, (a) di-ionic form, (b) mono-ionic form, (c) non-ionic form.

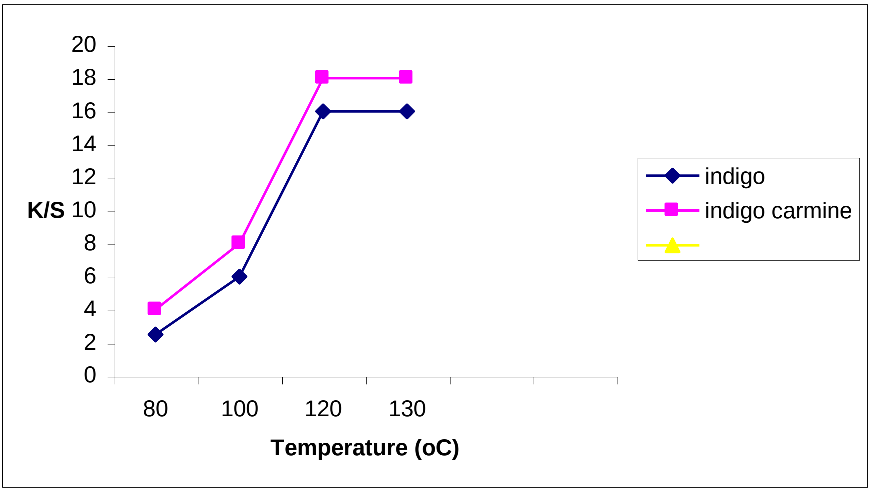

Figure 6, Effect of dyeing temperature on K/S values of polyester dyed samples. $Na_2S_2O_4$(8g/l), NaOH(1g/l), dye(2%owf), 40:1 bath ratio, dyeing time(30 min).

Table 2 and 3 show the reducing system effects on the values of pH, reduction potential (mV), and color strength expressed as K/S of cotton and polyester samples for indigo dyes. Obviously, no dye reduction takes place in FeSO4-NaOH system. FeSO4-NaOH bring about partial reduction of the dye. However, no dyeing occurs as evidenced by the no value of K/S. On the other hand, when both gluconic acid and dextrose systems were used, both dye reduction and dyeing take place ,with the gluconic acid system, Fe (II) complex was at its greatest concentration, causing complete reduction of indigo vat dye and good dyeing. Dextrose acts as a reducing agent in a basic solution and reduces the indigo dyes(19) .

These systems are capable of reducing indigo and keeping it in the reduced form thereby giving rise to good dyeing of cotton and polyester (20). This implies that indigo vat dyes can be reduced and maintained in the reduced form at low reduction potential (-700 mV). By using high temperature dyeing method, the two dyes under investigation dyed polyester at pH = 5 & 5.5 , K/S = 14 & 14.5 as shown in table 2 & 3, the dye uptake is less than obtained by FeSO4 - NaOH-Gluconic or dextrose-NaOH method and the hydro method. This may be attributed to the effect of the non ionic form of the dyes which can pentrate easily through polyester fiber and can not suffer from the negative charge on the fiber.

Table 2. : Effect of reducing system on pH, mV as well as K/S values of dyed samples (indigo dye1% shade, 40:1 bath ratio).

Dyeing System	Reduction potential and pH				K/S	
	Polyester		Cotton		Polyester	cotton
	pH	mV	PH	mV		
1- FeSO4 – NaOH.	5	-700	11.5	-700	-	-
2- FeSO4-NaOH-Gluconic	5.5	-700	11.5	-950	15.8	10.6
3- Dextrose- NaOH	5.6	-700	11.5	-950	16.5	16
4- Sodium hydrosulfite- NaOH	5.45	-700	11.7	-990	15.6	4.9
5- Under pressure	5	-700	-	-	14	-

Table 3. : Effect of reducing system on pH, mV as well as K/S values of dyed samples (indigo carmine dye1% shade, 40:1 bath ratio).

Dyeing System	Reduction potential and pH				K/S	
	Polyester		Cotton		Polyester	cotton
	pH	mV	PH	mV		
1- FeSO4 – NaOH.	5	-700	11	-650	-	-
2- FeSO4-NaOH-Gluconic	5.4	-700	11.5	-980	15.6	15
3- Dextrose- NaOH	5.6	-700	11.4	-960	16.5	16
4- Sodium hydrosulfite- NaOH	5.45	-700	11.5	-990	16	10.5
5- Under pressure	5.5	-700	-	-	14.5	-

Fastness properties

Fastness properties for polyester and cotton fabric dyeings dyed at 1% shade of indigo and indigo carmine are shown in table (4 & 5). Dry and wet rubbing fastness for polyester was superior to that for cotton. On the other hand, light fastness for polyester was inferior to that for cotton. Wash fastness was the same for both fabrics.

As is evident the wash fastness of the dyeings obtained using both gluconic acid and dextrose systems exhibit similar values indicating that the use of reducing systems containing Fe (II) and dextrose have practically no effect on the wash fastness properties of the dyeings. The same holds true for the light and rubbing fastness. The latter ranges from good to excellent.

Table 4. Fastness properties of indigo-dyed polyester and cotton fabrics, (1% shade, 40:1 bath ratio).

Dyeing system	Washing				Rubbing				Light	
	Polyester		cotton		Polyester		Cotton		Polyester	Cotton
	St	Cc	St	Cc	Dry	Wet	Dry	Wet		
1- Hydro	4	4	4	4	4-5	5	3-4	4	6	6-7
2- FeSO4 -Gluconic	5	4	4	4	5	5	4-5	5	6-7	7
3- Dextrose-NaOH	5	5	5	5	5	5	5	5	6-7	7
4- Under pressure	4-5	4	-	-	4-5	4	-	-	6	-

St : staining
Cc : color change

Table 5. Fastness properties of indigo carmine-dyed polyester and cotton fabrics, (1% shade, 40:1 bath ratio).

Dyeing system	Washing				Rubbing				Light	
	Polyester		cotton		Polyester		Cotton		Polyester	Cotton
	St	Cc	St	Cc	Dry	Wet	Dry	Wet		
5- Hydro	4	4-5	4	4-5	5	5	4-5	4	6-7	7
6- FeSO4 -Gluconic	6	4-5	4	4-5	5	5	4-5	5	6	7-8
7- Dextrose-NaOH	5	5	5	5	5	5	4-5	4-5	6-7	7
8- Under pressure	4-5	4	-	-	4-5	4	-	-	6	-

St : staining
Cc : color change

Conclusions

Dyeing polyester fabrics with indigo dyes is successful under certain conditions, which coordinate the rate of sodium hydrosulfite and sodium hydroxide. When the sodium hydrosulfite concentration is 8g/l, the optimum concentration of sodium hydroxide is 0.5g/l in the dyebath solution at 120°C. It seems that the role of non-ionic reduced indigo formation is important in this dyeing method. The dyeing temperature is effective, and well-dyed polyester fabrics are obtained at 120°C. The maximum wavelength of polyester fabrics dyed with indigo is clearly different from that of cotton fabrics. Polyester has a richer blue color than cotton when they dyed with indigo and indigo carmine. The rubbing fastness of polyester dyed with indigo dyes is superior to that of cotton.

Dextrose is also used for dyeing polyester and cotton successfully.

Polyester fabric could be successfully dyed with indigo dyes by Iron(II) salt complex as substitute for sodium hydrosulphite.

Dextrose was also used for dyeing polyester and cotton fabrics with indigo dyes with good results.

Polyester could be dyed with high temperature method but the dye uptake is less than obtained by $FeSO_4$ - NaOH-Gluconic or dextrose-NaOH method and the hydro method.

References :

1. PARMAR, M.S., SATSANGI, S.S., AND PRAKASH, J., Indigo Dyed Warp Yarn. An Essential Requirrenment Manufacturing Denium, Colourage 46, 45-50 (1996).
2. SAKAGAWA, T., KOSHIDA, H., AND NAKAYAMA, T., Proposal for New Application Methods of Indigo to Dyfashionable and Sensuous Beauty (1), Senshoku Kogyo., 39, 210-220 (1991).
3. KATSUSHI, K., SETSUAKI, H., AND SHINGO M., Dyeing Polyester Fabrics with Indigo., Textile Res., J., 75(2), 149-155 (2005).
4. KOSHIDA, H., AND NAKAYAMA, T., New Application Technologies of Vat Dye, Senshokukogyo 35(5), 199-225 (1987).
5. HONGYO, S., Dyeing Synthetic Fibers with Indigo Dyes, Senshoku Kogyo 47, 55-62 (1999).
6. SUGAWARA, H., Dyeing polyester fiber products with Indigo Dyes with High Color Depth and Brightness, Japanese Patent 09132879 (1997).
7. ROESSLER, A., CRETTENAND D, DOSSENBACH O. and RYS. P.J. Appl. Electrochem., 33: 901 (2003).

8. SEMET, B., SACKINGEN, B. AND GURNINGER G.E., New application technologies of vat dyes, Melliand Textilberichte , 76 (3), 161-164 (1995).

9. CHAVAN, R.B., and CHAKRABORTY, J.N. Dyeing polyester fabric with indigo, Coloration Technology., 117 (2) : 88- 94 (2001).

10. GOKHALE, V. and SHAH, R.C., Cotton Piece Dyeing, 1st edition, Ahmed Abad , Textite Industries Research Association, India, 30-35 (1974).

11. NAIR, G.P. , and TRIVEDI, S.S., Colorage, 17 (27), 19-21 (1970).

12. SHADOV, F., MORCHAGIN, and MATETSKY A., Chemidcal Technology of Fibrous Materials, in English (revised). Mir publishers, Moscow , 428 – 433 (1978).

13. FIETIG, D. and KONG, K., Textile Praxis, International,, 577-586 (1977).

14. JUDD D.B. and. WYSEZCHI, G., Color in Business, Science and Industry, 3rd Edn., Joh-n Wley &Sons; new York (1975).

15. BECHTOLD, T., et al., Journal of the Society of Dyers and Colourists, 113 (4) : 135-144 (1997).

16. HONGYO, S., Technology by Indigo Base Dyestuff, Shoku Kenkyu, 45, 30-35 (2001).

17. HONGYO, S., KUNITOU, K., and MAEDA, S., Dyeing of Synthetic Fiber Garments by Indigo Dyes, Okayama-Ken Ko- Gijutsu Senta Hokoku 25, 53-54 (1999).

18. KUROKI, N., " Senshokurironkagaku", 1st ed., Makisyoten, Japan, 41-42 (2001).

19. PAUL F., Indigo dye, J. of Chemical Education. 78(11), 160 (2001).

20. HONGYO, S., KUNITOU, K., and MAEDA, S., Dyeing of Synthetic Fibers with Vat Dyes, Senshoku Kogyo 48, 3-8 (2002).