

Dyebath Reuse in Dyeing of Nylon Microfiber Non-woven Fabric with 1:2 Metal Complex Dyes

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Abstract: Dyebath used for metal complex dyeing of nylon microfiber was recycled to reduce the overall amounts of metal complex dyeing effluents. Instead of discharging the dyebath after each dyeing cycle, the residual dyebath was analyzed spectrophotometrically and reconstituted to the required concentration of dyes and auxiliaries. Dyebaths were reused eight times and the CIELAB coordinates of dyed samples were measured after each recycling. Color difference (ΔE^*) between the sample dyed in the fresh bath and that from reused dyebath was maintained below 1.5. The levelness and fastness of dyed fabrics from recycled dyebath were not impaired either. Chromium content of each recycled dyebath was similar to that of the first residual dyebath.

Keywords: Dyebath reuse, Nylon microfiber, Metal complex dyes

Introduction

Compared with regular fiber yarns, microfibers have larger surface area that reflects higher proportion of incident light. The result is a visually lighter appearance. The fineness-related dye uptake property has been previously investigated by Fothergill[1]:

$$\frac{C_2}{C_1} = \sqrt{\frac{D_1}{D_2}}$$

where, C_1 and C_2 : concentrations of dye in fiber 1 and 2

D_1 and D_2 : denier of fiber 1 and 2

Since microfiber yarn has much larger surface area compared to normal one, more dyestuff is required to achieve a given depth of shade. Consequently, after the dyeing of nylon microfiber, effluent with higher levels of dye concentration is drained. Furthermore, metal complex dyes, which are used for high fastness dyeing of nylon microfiber, can cause serious environmental problems when they are discharged. The dyeing can also be unlevelled since the increased fiber surface can lead to earlier and faster dye uptake at the start of the dyeing process. The fastness of the dyed microfiber materials would be poor as well, especially in the dark shades, which is mainly the result of higher dye adsorption[2].

Dyebath reuse has long been recognized as a stratagem in pollution prevention and reduction of water, energy, and chemicals. The principle work on dyebath reuse has included the pilot scale dyeing of nylon carpet, nylon pantyhose, and package dyeing of polyester yarn. Batch dyeing of cotton knit fabric with reactive dyes and polyester, nylon, and acrylic with disperse dyes has been reported for laboratory scale[3-5].

In pilot scale experiments, dyebaths have been reused over 30 times[6]. A theoretical analysis of the impurity buildup in

recycling bath led to the conclusion that the buildup rate of auxiliary and chemical impurities slows down with each successive reuse and approaches a limiting value. However, levelness of dyeings were not considered in these experiments.

For dyebath recycling of direct dyes on cotton, presence of colored non-dyeing impurities can affect the measurement of residual dye concentration and metal ions in the water used have to be removed to obtain stable shades[7]. Recently, the effects of dye subclass, dye concentration, liquor ratio, and point of dye addition on levelness of reused direct dyebaths was examined[8].

In the present study, nylon microfiber non-woven fabric was dyed with 1:2 metal complex dyes in a dyebath reuse system. The objective of the study was to reduce the volume of water required, the quantities of effluent discharged, and the energy consumed during the dyeing of microfibers. Instead of discharging the dyebath after each dyeing cycle, the residual dyebath was spectrophotometrically analyzed and then reconstituted to the desired concentration of dyes and auxiliaries for a repeated dyeing. Color reproducibility, levelness and fastness of the dyed samples were measured after each recycling. Chromium residues of each recycled dyebath were checked with an ICP analyzer.

Experimental

Materials and dyeing method

Nylon microfiber non-woven fabric (Nylon 6, 0.07 den, 220 g/m², polyurethane resin treated), kindly supplied by Kolon (Korea), was used for dyeing. Newbon MG (nonionic, Kichang) was used as a leveling agent. Polyfix SPC (anionic, Kichang) and Sunmorl BK 20-T (non-ionic, Kichang) were also used as a fixing and a soaping agent respectively.

Nine commercial 1:2 metal complex dyes (Lanasyn series) of known chemical structures were supplied by Clariant and used without further purification. The dyes are listed in

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Table 1. 1:2 metal complex dyes used in dyeings

Type	Dye(Lanasyn)	C.I. No	λ_{max}
Non-sulphone	Grey BL	Acid Black 58	686
	Red 2GLN	Acid Red 404	486
	Yellow 2GLN	Acid Yellow 59	442
Mono-sulphone	Black S-GL	Acid Black 222	574
	Navy S-BL	Acid Blue 296	642
	Dark Brown S-GL	Acid Brown 194	468
Di-sulphone	Black S-DL	Acid Black 194	570
	Blue S-DNL	Acid Blue 193	578
	Brown S-DL	Acid Brown 402	476

Table 1 along with the number of sulfone groups, C.I. No. and λ_{max} . Laboratory grade of sodium acetate, acetic acid, sodium dihydrogen phosphate and disodium hydrogen phosphate were also used.

Dyeing was carried out in an Ahiaba Nuiance (Ahiba, Switzerland) laboratory-dyeing machine. The dyebath (120 ml) which contained 1:2 metal complex dye (15% o.w.f.) and 0.5 g/l of leveling agent (Newbon MG) was prepared. A nylon microfiber non-woven fabric sample (4 g) was then immersed in the dyebath and dyed for 60 min at 98°C. After dyeing, all the samples were given a fixation treatment (Polyfix SPC, 5% o.w.f., 80°C, 30 min) followed by washing, soaping (Sunmorl BK 20-T 1.0 g/l, soda ash 1.0 g, 30°C, 20 min) and, finally, air-drying. Dyebath exhaustion (%) was determined using a UV/Visible-spectrophotometer. Dyeing was performed at various initial pH ranges (pH 4.0, 5.0, 6.0, 7.0). Exhaustion (%) and residual dyebath pH were measured in order to investigate the pH dependence of exhaustion (%). Once the optimum dyeing pH was determined, dyebaths were reused in three different pH control methods as shown in Table 2.

Method I is a buffer system that resists the effects of extraneous influences which are capable of changing the pH, therefore, the pH of dyebath can be stabilized without additional acid adding. This system is usually based on two chemicals, namely a weak acid and its salt with a stronger base such as acetic acid-sodium acetate or phosphoric acid-sodium phosphate[9]. Method II is the most common pH control method, which is ideal to get a good dyeing reproducibility, however, the pH of dyebath should be readjusted with acetic acid for every dyebath reuse. Method III was used as a control to compare it with two other

Table 2. pH control methods used in dyebath recycling

pH control method	Initial pH adjustment	pH readjustment for the next dyeing
I	Buffer (sodium acetate-acetic acid)	None
II	Acetic acid	Acetic acid
III	Acetic acid	None

methods in the dyebath reuse system.

Dyebath reuse procedure

After dyeing, the dyebath was analyzed and reconstituted with the necessary amounts of dyes, auxiliaries and water. The addition of auxiliaries at a level commensurate with the fresh water necessary to maintain a constant liquor ratio of the original volume was found to be sufficient to permit several cycles of reuse. The dyebath was recycled eight times. After each recycle, the residual dyebath pH was measured. Amount of chromium in the residual dyebath was also measured using an ICP analyzer (ICPQ-1000, Shimadzu, Japan).

Measurement of color difference and levelness

Colors of the dyed samples were measured spectrophotometrically (Macbeth Color-Eye 3000, standard illuminant D65, 10° standard observer, and specular component included). CIELAB color differences (ΔE^*) between the fabrics dyed in the first dyebath and those from each reused dyebath were measured to assess the reproducibility of dyeing.

The levelness of dyed fabric was also assessed. Five points on a trial sample were measured at regular intervals and the mean value of the color differences between two points, which were systematically chosen out of five points, was then calculated.

Color fastness test

Color fastness was determined according to the Korean Industrial Standard procedures. Specific test methods used were: KS K 0430 A1 (color fastness to washing), KS K 0650 (color fastness to rubbing), and KS K 0464 (durability to dry cleaning). Changes in shade and staining were assessed using gray scales.

Results and Discussion

Metal complex dyes are applied to nylon in a manner similar to that used for acid dyes. Therefore, hydrophobic interactions between dye and fiber and ion-ion electrostatic interactions between dye anion and protonated amino groups of the fiber contribute to the dye-substrate substantivity[10]. In aqueous solution at neutral pH, nylon exists as a zwitterion structure ($^+NH_2$ -nylon- CO_2^-). Under acidic conditions the carboxylate anions are protonated, and the dye anions associate with the amino groups in a similar manner to the adsorption of dye on wool. The maximum quantity of dye capable of being adsorbed to these groups is approximately equivalent to the number of amino groups in the fiber[11]. Thus the relative contribution of ionic forces is governed by the pH of the dyebath, and is a major determinant in controlling the rate and extent of dye uptake.

The relationship between dye exhaustion (%) and dyebath pH is shown in Figure 1. As the pH of the dyebath is lowered

to 4.0, dye exhaustion (%) increases to 83% while there is a lower exhaustion around neutral pH. Thus the control of pH during the dyeing of nylon is very important to achieve a good dyeing reproducibility. Dyebath with pH less than 4 was not considered due to the problems of strike and unlevelness.

Having decided the optimum pH of dyebath as 4.0, dyebaths were reused using three pH control methods as described in Table 2 and the results are shown in Figure 2 and Figure 3. A comparison of residual dyebath pH for the three different pH control methods is given in Figure 2. The change of residual dyebath pH for control method I was sufficiently small, irrespective of dyebath reuse times. For method II, residual dyebath pH was kept just above 4, except for the residual dyebath of the first dyeing. The decrease of residual dyebath pH after the 2nd and 3rd dyeing can be

attributed to the formation of a buffer system between salt cations left after the adsorption of dye anion and acetic acid that was added to readjust the initial pH to 4.0 after each dyeing. Therefore, build-up of salt in the reused dyebath creates a buffer system that makes the change of dyebath pH difficult over the dyeing. The residual dyebath pH with method III increased consistently with the times of reuse.

Figure 3 shows the dye exhaustion (%) of C.I. Acid Black 194 at pH 4.0 with three different pH control methods as the dyebath reuse proceeds. The exhaustion (%) of dyeing with pH control method I was high and stable, irrespective of the dyebath reuse time. Method II shows somewhat lower and less stable exhaustion (%) than method I. The increase in the exhaustion (%) of dyeing in the 2nd and 3rd bath in comparison with dyeing in the fresh bath is consistent with the results of residual dyebath pH. The exhaustion (%) with

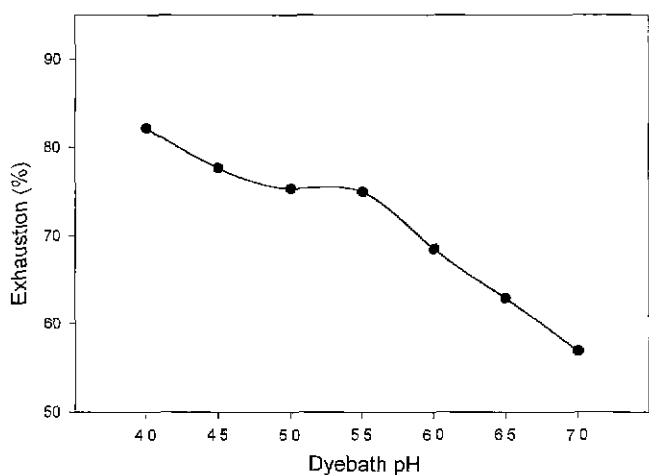


Figure 1. Exhaustion (%) of C.I. Acid Black 194 at various dyebath pH values (pH adjustment with acetic acid).

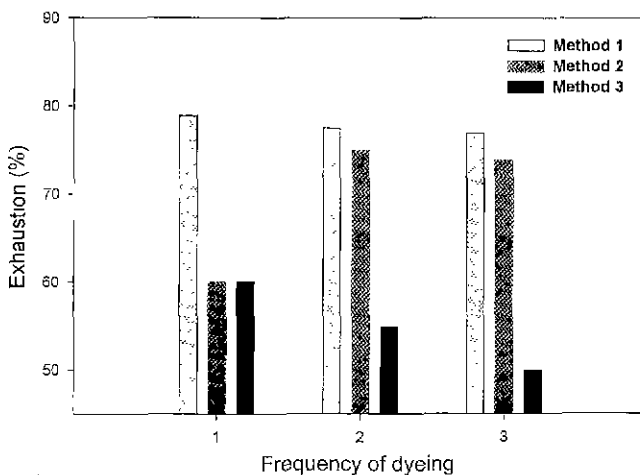


Figure 3. Exhaustion (%) of C.I. Acid Black 194 with various pH control systems as dyebath reuse proceeds (initial pH 4.0).

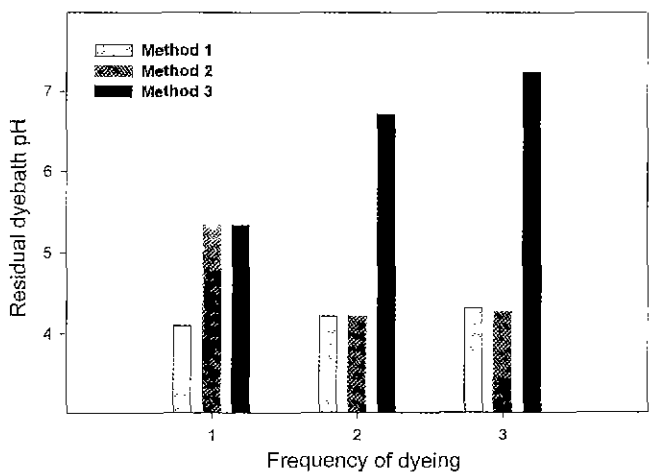


Figure 2. Residual dyebath pH with various pH control systems as dyebath reuse proceeds (C.I. Acid Black 194, initial pH 4.0).

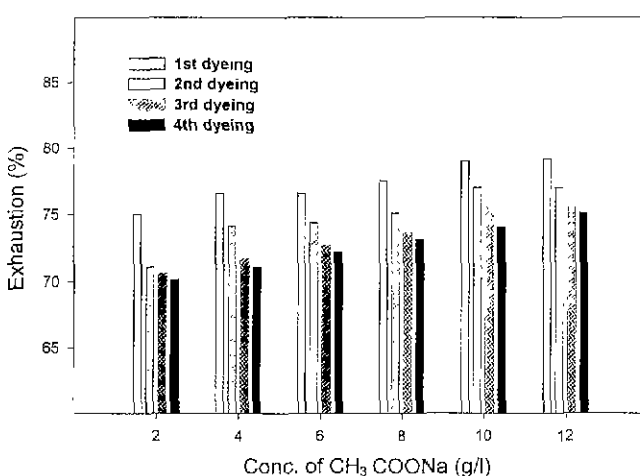


Figure 4. Exhaustion (%) of C.I. Acid Black 194 with various buffer concentrations as dyebath reuse proceeds (initial pH 4.0).

method III was very low and decreased with the time of reuse. These results can also be explained based on the residual dyebath pH change (Figure 2).

For dyeings in the buffer solution, the exhaustion (%) is dependent on the sodium acetate concentration and dyebath

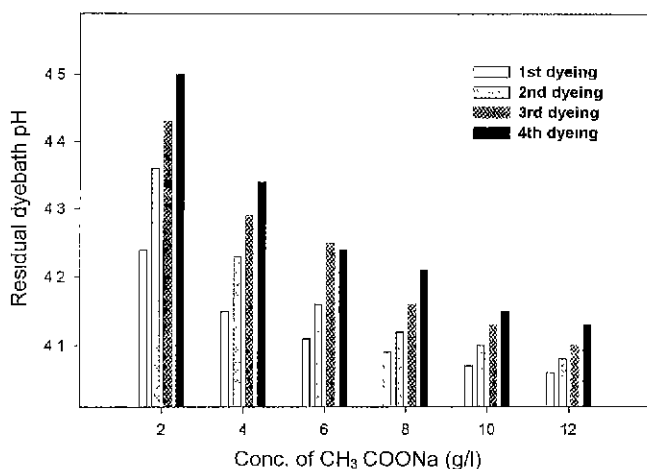


Figure 5. Residual dyebath pH with various buffer concentration as dyebath reuse proceeds (C.I. Acid Black 194, initial pH 4.0)

reuse time. Figure 4 shows that the exhaustion (%) of dyeing increases with concentrations of sodium acetate and decreases as dyebath reuse proceeds.

Figure 5 shows the effect of buffer capacity of sodium acetate on the residual dyebath pH. The higher the concentration of sodium acetate, the smaller the variation of residual dyebath pH as dyebath reuse proceeds. For example, 12 g/l sodium acetate gives a residual pH value of 4.06~4.13 while 2 g/l sodium acetate gives a value of 4.24~4.50. Consequently, dyebath exhaustion and reproducibility of dyeing increase with the concentration of sodium acetate.

The overall color differences of dyed fabrics between the first and reused dyeings are shown in Table 3. After eight reuse cycles, color consistency of dyeings remained acceptable. The color differences between dyeings in the first dyebath and those from reused dyebaths range from 0.11 to 1.6 CIELAB unit which are hard to distinguish with human eyes. In particular, the dyes which contained no sulfone group show better color reproducibility and levelness due to higher exhaustion (90~95%) and migration properties than those containing one or two sulfone groups.

Levelness is the uniformity of dye distribution on the fabric. Two fundamental mechanisms contribute to the levelness of

Table 3. Color differences (ΔE^*) of dyed fabrics between the first and reused dyeings (pH control; Method I, 10.0 g/l of sodium acetate, initial pH 4.0)

Dye	Dyebath Reuse No.	Dyeing Cycle						
		2 nd	3 rd	4 th	5 th	6 th	7 th	8 th
Non-sulphone	Black 58	0.11	0.50	0.59	0.56	0.61	0.71	0.49
	Red 404	0.44	0.40	0.84	0.88	0.98	0.52	0.63
	Yellow 59	0.4	0.83	0.73	0.83	0.79	1.30	0.77
Mono- sulphone	Black 222	0.70	0.60	0.40	0.30	0.30	0.40	0.80
	Blue 296	0.60	0.90	1.50	1.10	1.60	1.60	1.20
	Brown 194	0.60	1.40	1.00	1.00	0.90	1.40	1.05
Di-sulphone	Black 194	0.30	1.20	0.30	1.00	1.00	0.40	1.30
	Blue 193	0.60	0.40	0.20	0.60	0.80	0.90	0.40
	Brown 42	0.60	1.30	0.30	0.70	0.30	1.30	0.60

Table 4. Averaged color differences (ΔE^*) of dyed fabrics (C.I. Acid Black 194, pH control; Method I, 10.0 g/l of sodium acetate, initial pH 4.0)

Measure No.	Dyebath Reuse No.	Dyeing Cycle							
		1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th
1		0.20	0.32	0.39	0.30	0.17	0.50	0.45	0.24
2		0.12	0.33	0.10	0.30	0.22	0.29	0.06	0.04
3		0.11	0.04	0.16	0.08	0.12	0.20	0.47	0.21
4		0.17	0.17	0.13	0.44	0.08	0.27	1.00	0.31
5		0.01	0.65	0.34	0.14	0.06	0.20	0.20	0.08
6		0.11	0.32	0.45	0.11	0.10	0.08	0.33	0.28
7		0.37	0.0	0.33	0.43	0.14	0.19	0.85	0.85
8		0.10	0.33	0.11	0.14	0.27	0.69	0.50	0.61
9		0.30	0.20	0.05	0.17	0.05	0.48	1.00	0.82
10		0.30	0.20	0.12	0.08	0.14	0.45	0.50	0.50

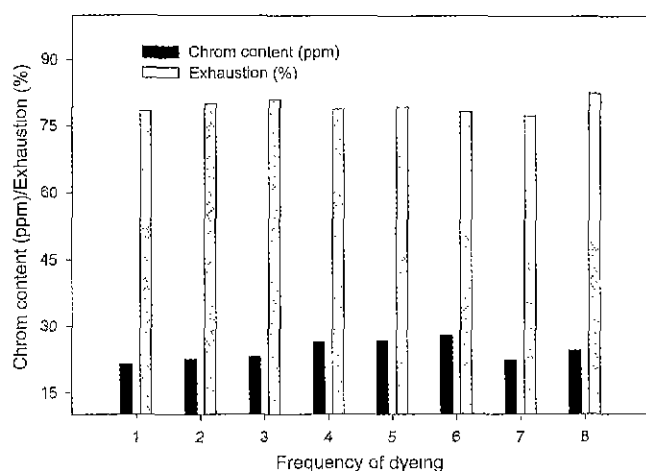


Figure 6. Exhaustion (%) and chromium residues as dyebath reuse proceeds (C.I. Acid Black 194, pH control; Method I, 10.0 g/l of sodium acetate).

batch dyeing. One is the initial sorption of dye, the other is the migration of dye after its initial sorption on the fiber[12]. Table 4 shows the levelness achieved over successive reuses are good in the dyeing of nylon microfiber non-woven fabric with C.I. Acid Black 194. Since C.I. Acid Black 194 contains two sulfone groups, it would be expected to show the worst levelness properties of all the dyes. The mean values of the color differences are less than one CIELAB unit and the levelness was maintained through eight reuses.

Figure 6 shows the exhaustion (%) and chromium residues of each recycled residual dyebath. Each reused dyebath had similar chromium content of around 25 ppm. This means that chromium does not accumulate in the residual dyebath. The amount of chromium discharged could consequently be reduced in proportion to the dyebath reuse frequency.

Tables 5, 6, and 7 show the results of color fastness to washing, rubbing and durability to dry cleaning, respectively, for dyed nylon microfiber non-woven fabrics with C.I. Acid Black 194. The ratings for color fastness to washing

Table 5. Color fastness of dyed fabric to washing (KS K 0430 A-1, C.I. Acid Black 194, pH control: Method I, 10.0 g/l of sodium acetate, initial pH 4.0)

Dyebath Reuse No.	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th
Change	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Stain	Wool	4	4	4	4	4	4	4
	Nylon	1-2	1-2	1-2	1-2	1-2	1-2	1-2

Table 6. Color fastness of dyed fabric to rubbing (KS K 0650, C.I. Acid Black 194, pH control: Method I, 10.0 g/l of sodium acetate, initial pH 4.0)

Dyebath Reuse No.	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th
Stain(Dry)	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4
Stain(Wet)	2	2	2	2	2	2	2	2

Table 7. Durability of dyed fabric to dry cleaning (KS K 0464, C.I. Acid Black 194, pH control, Method I, 10.0 g/l of sodium acetate, initial pH 4.0)

Dyebath Reuse No.	1 st	3 rd	6 th	8 th
Change	4-5	4-5	4-5	4-5

were all the same to that of the first dyeing. Color fastness to washing was generally good or moderately good except for staining on nylon (color change 4-5, staining on wool 4, staining on nylon 1-2). Durability to dry cleaning of all the fabrics dyed in the reused dyebath was good as well. In the case of the color fastness to rubbing, the ratings of staining of dry samples were 3-4 while those for wet samples were 2. These results clearly show that no deterioration of the color fastness occurs over the series of dyebath recycled dyeings.

Conclusions

In the dyebath reuse system, control of dyebath pH with a buffer system was most important to obtain dyeings of high reproducibility. While the final pH increases and exhaustion of the dyebath decreases slightly as reuse proceeds, the reconstitution of the dyebath to the original level allows for consistent shades. After eight cycles of reuse, the levelness and color consistency of dyeings were acceptable. The color differences between the dyeings in the original dyebath and those from reused dyebaths ranges from 0.11 to 1.6 CIELAB unit. In addition, no deterioration in color fastness occurred over eight cycles of reuse. Residual amounts of chromium did not increase either with dyebath recycling.

Provided that dyes and dyeing auxiliaries were properly analyzed and replenished, and that the dyebath pH were controlled through the cycle-to-cycle, metal complex dyebath reuse in the coloration of nylon microfiber non-woven fabric represents a feasible and economic route to reduce energy and materials consumption without sacrificing the quality of the finished goods.

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