

가수분해된 반응성염료의 재사용에 관한 연구

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A Study in Reuse of Hydrolyzed Reactive Dyes

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Abstract

가수분해된 네 개의 반응성 염료를 이용하여 견, 양모, 나일론 섬유를 염색할 때 영향을 미치는 여러 인자들에 대하여 연구하였다. 염의 투입을 가수분해 전과 후로 달리하였을 때 염색된 직물의 K/S 값에 미치는 영향이 다르게 나타났다. 또한 K/S 값에 미치는 염의 영향은 염료와 직물의 종류에 따라 각기 달랐으며 염의 영향은 염료의 분자 크기가 클 때 더 크게 나타났다. 이는 염 농도의 증가시 염욕 안에서의 염료 용해도가 염료 분자가 클 때 더 많은 영향을 받기 때문인 것으로 생각된다. 욕비 증가 시에는 염색된 직물의 K/S 값은 초기에 감소를 보이다가 높은 욕비에서 K/S 값이 증가되었는데 이는 염의 농도의 감소로 인한 영향으로 사료된다. 가수분해된 반응성 염료로 염색된 직물의 수세 견뢰도는 염료의 분자 크기에 의해 영향을 받았으며 직물의 마찰, 땀 견뢰도는 Gray scale에서 3보다 높았다. 본 연구의 결과는 면 섬유 염색에 사용한 가수분해된 반응성 염료를 이용하여 견, 양모, 또는 나일론 섬유의 염색에 재 사용할 수 있는 가능성을 제시하여 준다.

Key words: hydrolysis, reactive dye, dye reuse : 가수분해, 반응성 염료, 염료 재사용

I. Introduction

Reactive dyes are one of the most widely used dyes due to their excellent wash colorfastness and convenient application process^{1, 2)}. Nevertheless, total exhaustion of the reactive dyes during cellulose dyeing is not very high, i.e., 50-90%. This means that up to 50% of total dye undergoes

hydrolysis and is discharged into the effluent system³. After the dyeing, therefore, unfixed or hydrolyzed reactive dyes have to be washed off thoroughly to achieve desirable superior wash colorfastness⁴⁾. In addition, during reactive dyeing tremendous amounts of salt is required to increase affinity of the dye toward cellulosic fibers and to aid exhaustion to the maximum level⁵⁾. Therefore, it was reported that "reactive dyes pose the main problem in color cleaning for dyeing effluent"⁶⁾.

Due to increasing environmental concerns and the resultant stringent regulations that exist

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worldwide, reactive dyers must ensure minimal or zero pollution by reducing or removing residual dyes and other pollutants such as salt⁷⁾. Three methods are generally available for such reductions: wastewater treatment by using filtering(nanofilter) or chemical treatment (ozonolysis, chlorine treatment), minimizing waste source by reducing the required amounts of dyes and salt(continuous process), and dyebath reuse¹⁾.

The use of nanofilter membrane in treatment of wastewater allows a separation of large molecules such as reactive dyes and auxiliaries from the relatively small water and sodium chloride molecules⁵⁾. Selective oxidation of dye chromophores by using chlorine and ozone gas can permit reuse of dye wastewater containing salt for further dyeing. However, such a dye degradation process could produce unknown toxic and/or mutagenic/carcinogenic fragmentation by oxidative breakdown⁵⁾. Therefore, the implementation of such process must require a complete fate analysis of dye molecules after degradation.

On the other hand, direct dyebath reuse promises several advantages: low capital cost for implementation of the technology, substantial processing cost savings, significant environmental benefits, potential for widespread use^{5, 9-11)}.

The dyebath reuse results not only in cost savings from reduced water, chemical and energy expenditures, but it also decreases the volume of

discharged wastewater and pollutants^{5, 9-11)}.

Reuse of spent reactive dyebath in cellulosic fiber dyeing has been examined in several studies^{7, 12)}. However, due to the presence of hydrolyzed dyes the reuse of the reactive dyebath in cellulosic fiber dyeing generally leads to poor wet colorfastness¹⁾. Once the reactive dyes are hydrolyzed, they could act like an ordinary acid dye. This means that these hydrolyzed dyes in the spent reactive dyebath could be reused in dyeing of positively charged fibers such as wool, silk, and nylon in a suitable condition. Therefore, the purpose of the present study is to investigate the feasibility of using the hydrolyzed reactive dyes in dyeing of wool, silk, and nylon.

II. Experimental

1. Materials

Fabrics used in this study included cotton plainweave, wool worsted gabardine, silk habutae, and nylon plainweave. Four reactive dyes used in the present study are listed in Table 1. Criteria for dye selection were kinds of functional groups, number of solubilizing groups, and size of the dye molecule. These dyes were directly used without any further purification. Other chemicals such as anhydrous sodium carbonate(Duksan Co., Ltd.), NaOH(Yakuri Chemicals, Co., Ltd.), and sodium chloride(Duksan Pure Chemicals, Co., Ltd.) were

Table 1. Specifications of reactive dyes used

Name of the dyes (commercial name)	Reactive group	Molecular weight	Number of -SO ₃ H	Manufacturer
C.I. Reactive Blue 4 (Procion Blue MX-R)	dichlorotriazine	524.9	1	BASF
C.I. Reactive Red 120 (Procion Red HE3B)	two groups of monochlorotriazine	1324.1	6	BASF
C.I. Reactive Blue 182 (Cibacron Blue F-R)	monochlorotriazine	677.6	2	Ciba-Geigy
C.I. Reactive Blue 19 (Remazol Brilliant Blue R)	vinylsulfone	525.1	1	Bayer

reagent grade.

2. Prehydrolysis

Prehydrolysis of the reactive dyes was carried out as follows: The reactive dye (2% on the weight of fiber, owf) was hydrolyzed at 90°C for 45 min in Ahiba Dyeing Apparatus. The bath also contained 10% owf Na_2CO_3 and 4% owf NaOH. The salt (NaCl) was also added in the bath prior to the hydrolysis. The concentrations of salt were varied as 0, 5, 10, 15, 20, and 25% owf. After hydrolysis, the bath was allowed to cool down to 25°C and the pH of the bath was adjusted to 3 by adding appropriate amounts of 10% HCl solution. This would simulate conventional dyeing of wool, silk, and nylon with acid dyes. Unless otherwise noted, salt was added to the dyebath before hydrolysis. For comparison, the salt was added after hydrolysis in some cases.

3. Dyeing

In order to confirm completion of hydrolysis of the reactive dyes at the condition described above, cotton fabric was dyed with the hydrolyzed reactive dyes. The cotton was added at 50°C and the bath was boiled to 100°C for 30 min followed by one hour additional dyeing at boiling. The fabric was rinsed in a running water for 30 min. For silk, wool, and nylon the fabric was placed in the dyebath at 50°C and the temperature was raised to 90°C for 30 min followed by an additional one hour dyeing at 90°C.

After dyeing K/S values of the dyed fabrics were measured by using visible spectrophotometer (Macbeth Color Eye 7000) according to the following Kubelka–Munk equation:

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

where R is the reflectance of the dyed fabric at the wavelength of maximum absorption.

4. Colorfastness Evaluation

Colorfastness to washing was evaluated by Launder-Ometer (AATCC 61-1989) at 40°C for 45 min with multifiber fabric attached onto the dyed fabric. Detergent was used according to K/S M2715 at mild alkaline condition (pH 9.0–10.6). Perspiration tester (AATCC 15-1989) was used to measure perspiration colorfastness. Acidic perspiration was prepared according to AATCC method as follows: L-histidine hydrochloride monohydrate, D, L-lactic acid, disodium hydrogen phosphate (Na_2HPO_3) and NaCl. Crocking colorfastness was measured by using motorized crockmeter (Atlas) according to AATCC 8-1989. Gray scales for color change and staining were used to determine color changes of the dyed fabrics and staining on the multifiber fabrics.

III. Results and Discussion

K/S values of cotton fabrics dyed with hydrolyzed Reactive Blue 4 containing 0%, 5%, 15%, and 25% salt in the bath were 0.16, 0.21, 0.15, and 0.15 at 600 nm, respectively. These results confirm a complete hydrolysis of the reactive dyes at such a condition.

1. Effect of Salt Concentration

Fig. 1 shows the effect of NaCl concentration on K/S value of silk fabrics dyed with hydrolyzed Reactive Blue 4. In one set of the experiments, salt was added in the dyebath prior to the hydrolysis process to simulate conventional reactive dyeing since most of spent reactive dyebaths contained substantial amounts of salt. With a slight initial decrease in K/S values at 5% and 10% salt concentrations, K/S values considerably increased at high salt concentrations. Note that certain amounts of salt should be present even in

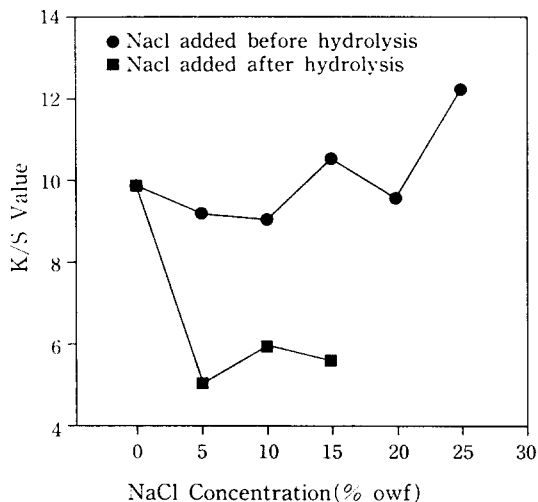


Fig. 1. Effect of NaCl concentration on K/S value of the silk fabric dyed with hydrolyzed Reactive Blue 4.

the bath without added salt due to the reaction between alkali added during the hydrolysis and the HCl used for pH control after hydrolysis.

On the other hand, when salt was added after hydrolysis process, K/S values of the dyed silk fabrics were substantially lower than that of the silk fabric dyed in the bath without added salt (Fig. 1). Only 5% salt addition was needed to reduce K/S value of silk by 50%. Since the hydrolyzed reactive dyebath usually contained salts, no further attempt was made to introduce salts after hydrolysis.

To study the effect of salt concentration in the hydrolyzed reactive dyebaths in more detail three additional dyes were further examined with silk fabrics, as shown in Fig. 2 In all the cases the presence of salt in the hydrolyzed dyebaths increased K/S values of the silk fabrics dyed with hydrolyzed reactive dyes. Effect of varying salt concentration was more prominent with hydrolyzed Reactive Red 120, whereas with hydrolyzed Reactive Blue 19, K/S values leveled off after an initial increase by salt addition.

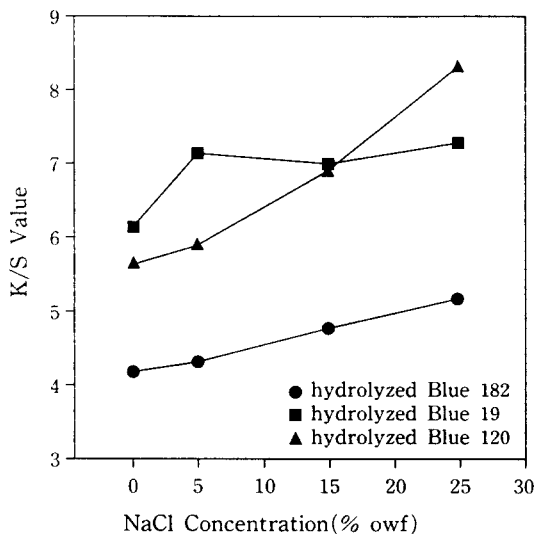


Fig. 2. Effect of NaCl concentration on K/S value of the silk fabric dyed with hydrolyzed reactive dyes.

However, unlike hydrolyzed Reactive Blue 4, no initial decrease was shown at low salt concentration.

Now wool fabrics were dyed with hydrolyzed reactive dyes and the results are illustrated in Fig. 3 In all the cases, K/S values of wool dyed with three pseudo-acid dyes were considerably greater than those of silk dyed with the same dyestuffs. The high K/S values of the dyed wool could be related to several reasons: the presence of a much larger number of reactive cationic groups in wool than silk, different optical characteristics of wool and silk, and different fixation ratios of the dyes in wool and silk¹⁾. Wool fabrics dyed with hydrolyzed Reactive Blue 182 and Reactive Red 120 showed increased K/S values with increasing salt concentration, but the effect was more prominent with hydrolyzed Reactive Red 120 as in the case of silk. On the other hand, no substantial variation of K/S values was observed when wool was dyed with hydrolyzed Reactive Blue 19.

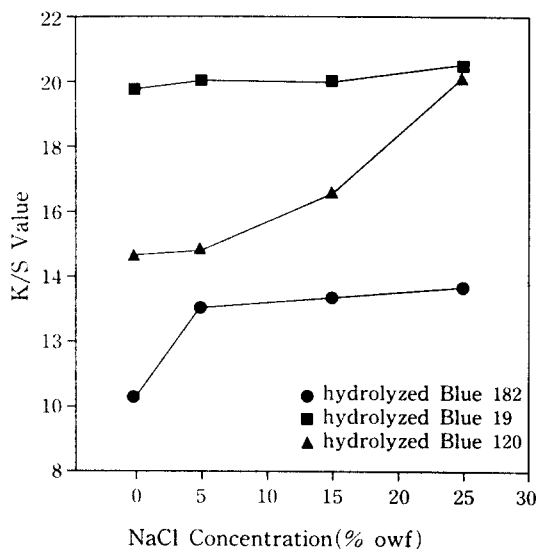


Fig. 3. Effect of NaCl concentration on K/S value of the wool fabric dyed with hydrolyzed reactive dyes.

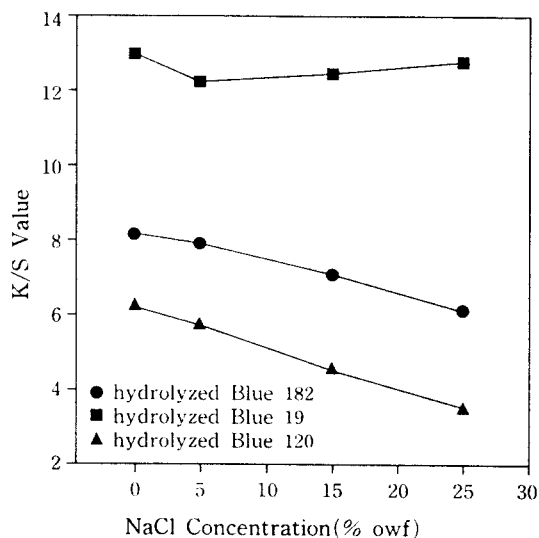


Fig. 4. Effect of NaCl concentration on K/S value of the nylon fabric dyed with hydrolyzed reactive dyes.

Fig. 4 represents K/S values of nylon dyed with the hydrolyzed reactive dyes in the presence of various amounts of salt. Interestingly, salt effects are now reversed, i.e., K/S values decreased with increasing salt concentration. Again nylon dyed with hydrolyzed Reactive Blue 19 showed somewhat different trends with other two dyes, i.e., relatively consistent K/S values at various salt concentrations. K/S values of nylon fabrics dyed with hydrolyzed Reactive Blue 182 and Reactive Blue 19 were lower than those of wool and higher than those of silk, but with hydrolyzed Reactive Red 120 K/S values of nylon were lower than those of wool and silk.

Results demonstrated that the dyeing of cationic fibers such as silk, wool, and nylon by using hydrolyzed reactive dyes was not governed by a simple mechanism. Combined effects of three important variables, i.e., characteristics of dyes, salt concentration, and fiber, were observed during dyeing with hydrolyzed reactive dyes. It is not

clear why the presence of salt during the hydrolysis increases sorption of dyes on silk and wool, whereas addition of salt after hydrolysis during dyeing of these fibers decreases dye sorption.

It is well known that the presence of salt decreases ionic interaction between anionic dye and cationic fiber in the dye bath¹³⁾. This consequently decreases dye sorption. Dyeing of silk by the hydrolyzed reactive dyes with salt added after hydrolysis (Fig. 1) and dyeing of nylon with salt added before hydrolysis (Fig. 4) followed this known mechanism. On the other hand, addition of salt prior to hydrolysis tended to show an opposite trend. This unexpected increase in sorption of dyes at a higher amount of salt prior to hydrolysis process made us suspect that there might be some physical change of salt during hydrolysis, i.e., ease of ionization. Another plausible explanation is that the presence of salts during hydrolysis would facilitate hydrolysis of reactive dyes. However, a further study would be needed

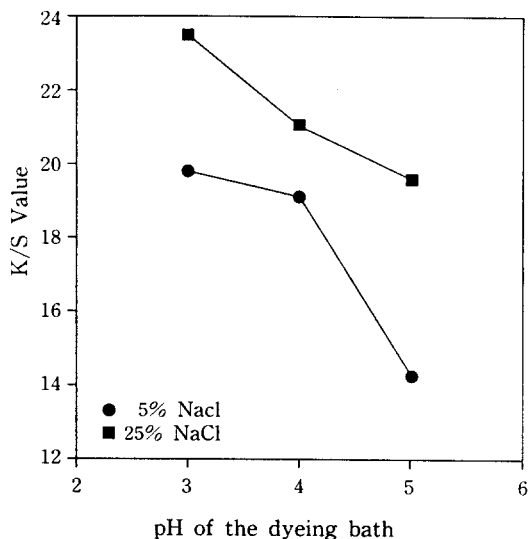


Fig. 5. Effect of pH on K/S value of the wool fabric dyed with hydrolyzed Reactive Red 120.

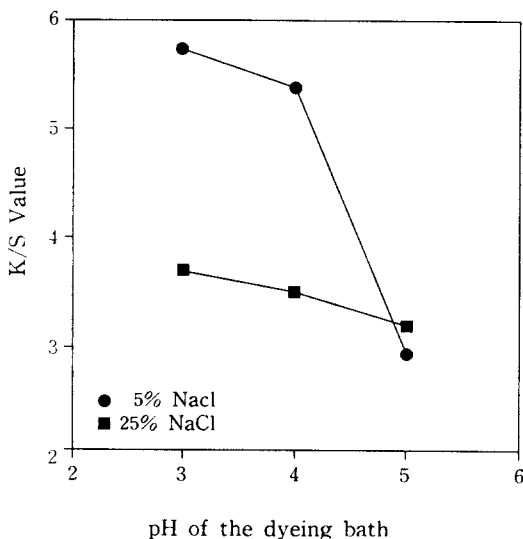


Fig. 6. Effect of pH on K/S value of the nylon fabric dyed with hydrolyzed Reactive Red 120.

to confirm the fate of salt during the hydrolysis and the effect of salt on the rate of reactive dye hydrolysis.

In the case of silk and wool, effects of salt addition prior to hydrolysis were the most prominent with hydrolyzed Reactive Red 120 (Fig. 2 and 3). This particular dye has an extremely high molecular weight (Table 1). Such a high molecular weight dye has high affinity toward cationic fibers due to the presence of non-ionic binding interactions between the dye molecule and the fiber such as dipoles, hydrogen bonding, and van der Waals forces. Since chloride anions and dye anions are competing for the same cationic sites in the fiber, sorption of chloride anions was expected to be faster than dye anions at an initial stage of dyeing. But at a later stage of dyeing, the large molecular dyes would be able to displace chloride anions easily due to additional non-ionic binding interactions¹³⁾. The presence of salt would facilitate sorption of the large molecular dyes into the fiber by decreasing dye solubility in the bath,

resulting in changing direction of equilibrium toward fiber. On the other hand, the presence of salt would have much less influence on solubility of small molecular dyes. Therefore, hydrolyzed Reactive Red 120 presumably behaves like conventional milling acid dyes while other small molecular weight dyes behave like leveling acid dyes.

2. Effect of Bath pH

Hydrolyzed Reactive Red 120 was selected to elucidate effect of bath pHs on K/S values of the dyed fabrics. As shown in Fig. 5 and 6, wool and nylon fabrics were dyed with hydrolyzed reactive dyes at two different levels of salt concentration which had been added before hydrolysis. For both wool and nylon fabrics, increase in the bath pH generally decreased K/S values of dyed fabrics. However, the effect was more considerable at low salt concentration. It is known that at low salt concentration effect of isoelectric point on dyeing of protein fiber is more substantial than at high

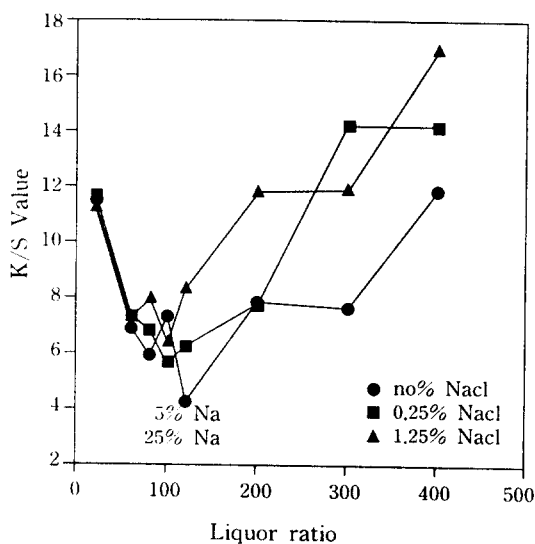


Fig. 7. Effect of liquor ratio on K/S value of the wool fabric dyed with hydrolyzed Reactive Red 120.

salt concentration¹³). These high K/S values at low pH can be mainly caused by increase in the positively charged dyeing sites in wool and nylon at low pH.

3. Effect of Liquor Ratio

While keeping amounts of the hydrolyzed Reactive Red 120 and salt concentration constant, liquor ratios of the dyeing bath have been varied from 20:1 to 400:1 by adding appropriate amounts of distilled water. Fig. 7 indicates that K/S value of the dyed fabric changed with changing the liquor ratios. There was an initial decrease in K/S values of the dyed wool with increasing liquor ratio, but at extremely higher liquor ratio K/S values showed maximum at each salt concentration. Increase in K/S value of dyed fabric at high liquor ratio has been also observed in the previous study¹¹). Such effects are generally more significant at high salt concentration. Increasing the liquor ratio changes the concentrations of dye and salt in the bath although their concentrations

based on the weight of fabric are constant. In general, the decrease in dye concentration would decrease dye sorption, whereas the decrease in salt concentration would increase dye sorption. Therefore, at high salt concentrations, effect of decrease in salt concentration could overcome effect of decrease in dye concentration, resulting in higher K/S values. Spectroscopic determination indicated that the actual dye concentration in the dyebath was only about 0.01g/L at 400:1 liquor ratio. Nevertheless, wool fabrics were dyed to high K/S value.

4. Colorfastness

In addition to K/S values, colorfastness of the dyed fabric is a very important factor in determining usability of the hydrolyzed reactive dyes. As shown in Table 2, in certain cases very poor wash fastness was obtained: silk fabrics dyed with hydrolyzed Reactive Blue 182 and 19, and wool fabrics dyed with hydrolyzed Reactive Blue 19. Contrarily, the fabrics dyed with hydrolyzed Reactive Red 120 showed excellent wash fastness. This high wash fastness seems to be related to the large molecular size of Reactive Red 120, which behaves like milling acid dye.

Table 3 shows crocking and perspiration fastnesses of the fabrics dyed with the same pseudo-acid dyes. Unlike wash fastness, crocking fastnesses of the silk, wool, and nylon fabrics were excellent with all three hydrolyzed reactive dyes at varying concentration of salts in the dyebaths. Effect of dyes on perspiration fastness varied by the kinds of fabric and salt concentration. Further colorfastness examination will be necessary with a wide range of dyes for a practical use.

IV. Conclusions

Four reactive dyes were hydrolyzed and reused

Table 2. Wash fastness of the fabrics dyed with hydrolyzed reactive dyes

Fabric	Dye ^a	Salt concentration											
		0 %			5%			15%			25%		
		A ^b	B ^c	C ^c	A	B	C	A	B	C	A	B	C
silk	R 120	5	4-5	5	5	4-5	5	5	4-5	5	5	4-5	5
	B 182	2	4	5	2	4	5	2	4	5	2	3-4	5
	B 19	2	4-5	2	2	4-5	2	2	4-5	2	1-2	4	2
wool	R 120	4-5	2	5	4	2	5	4	2	5	4	2	5
	B 182	4-5	2	5	4-5	2	5	4-5	2-3	5	4-5	2-3	5
	B 19	3	3	1-2	3	2-3	1-2	3	3	1-2	3	3	1-2
nylon	R 120	5	5	5	5	5	5	5	5	5	5	5	5
	B 182	5	5	5	5	5	5	5	5	5	5	5	5
	B 19	4-5	4-5	3	4-5	4-5	3	4-5	4-5	3	4-5	4-5	3

^a Hydrolyzed dyes : Reactive Red 120, Reactive Blue 182, and Reactive Blue 19. ^b color change of the dyed fabric.

Table 3. Crocking and perspiration fastnesses of the fabrics dyed with hydrolyzed reactive dyes

Fabric	Dye ^a	Crocking fastness				Perspiration fastness			
		Salt concentration							
		0%	5%	15%	25%	0%	5%	15%	25%
silk	R 120	5	5	5	5	4	3-4	4-5	4
	B 182	5	5	4-5	4-5	3-5	4-5	3	3
	B 19	5	5	5	5	3-4	3-4	3-4	3-4
wool	R 120	4-5	4-5	4-5	4-5	3	3	3-4	3-4
	B 182	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	B 19	4-5	4-5	4-5	4-5	3-4	3-4	3-4	3-4
nylon	R 120	5	5	5	5	4-5	4-5	4-5	4-5
	B 182	5	5	5	5	4-5	5	5	5
	B 19	5	5	4-5	5	3-4	3-4	3-4	3-4

^a The notation is the same as Table 2.

for dyeing silk, wool, and nylon fabrics. Following conclusions can be obtained from the present study.

1. The effect of salt addition before and after hydrolysis on K/S value of the fabrics dyed with hydrolyzed Reactive Blue 4 was completely different. The presence of salt during the hydrolysis tended to increase K/S values of the fabrics dyed with hydrolyzed reactive dyes, whereas addition of salt after hydrolysis decreased

their K/S values.

2. Varying the salt concentration prior to the hydrolysis significantly influenced on K/S values of the dyed fabrics. This effect varied by the kinds of dyes and fabrics. Increasing the salt concentration increased K/S values of the dyed silk and wool, but decreased those of dyed nylon. Increase(silk and wool) and decrease(nylon) in K/S values of the dyed fabrics were most prominent with hydrolyzed Reactive Red 120,

presumably due to its high molecular weight affecting on solubility of the dye in the bath.

3. As expected, K/S values of the dyed fabrics were higher at low pHs than those of the fabrics dyed at high pHs.

4. Increasing the liquor ratio also changed K/S values of wool fabrics dyed with hydrolyzed Reactive Red 120, due to decrease in concentrations of dye and salt.

5. Wash fastness is largely dependent upon the molecular size of the dyes. Wash fastness of hydrolyzed Reactive Red 120 with large molecular size was much higher than that of hydrolyzed Reactive Blue 19 with small molecular size. Crocking and perspiration fastnesses were higher than 3 on the Gray scale in all the cases. Therefore, it could be concluded that the reuse of hydrolyzed reactive dyes is feasible in dyeing silk, wool, and nylon and these dyes behave like leveling or milling acid dyes depending upon their molecular structure. A further study would be needed to examine the fate of salt during hydrolysis in order to investigate mechanism of hydrolyzed reactive dyeing.

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