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Evaluation of dye-ability and harmfulness of the reactive dyes replacing the metallic acid dyes for wool+

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Abstract

Metal acid dyes are usually used to dye wool fabric to achieve high concentrated color and strong color fastness. However, metal acid dyes contain lots of heavy metal. That causes not only environmental pollution but also diseases to human.

In this study, wool reactive dyes instead of metal acid dyes for wool, which are environmental friendly, are compared and analyzed in the evaluation system of their harmfulness, containing heavy metals and examined exhaustion rates and dyeing characteristics.

Key Words : reactive dyes, heavy metal, harmfulness, metal dyes, wool

Ⅰ. Introduction

In recent years, there have been reports in new pertaining to heavy metals and various harmful substances which have been detected in agricultural and marine products. Over the course of our lives, heavy metals are accumulated in the human body through food. In addition, various finish materials and smells from chemicals cause a kind of 'Sick House Syndrome', which threatens our living environment[1]. They were detected even in interior materials of transportation including a lot of fabric products. Moreover, toys for kids also are exposed to the heavy metals and harmful substances and cannot provide healthy environment. This is the actuality and none of food, clothing and shelter is secured for health and safety[2].

With invasion of heavy metals and harmful substances into our lives, the threat of heavy metals has reached dangerous levels even in many of the clothes we wear. In addition, from

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underwear which is always in contact with the human body to outer garments and even in fabric accessories such as mufflers, the heavy metals were detected and are known to cause various allergies, which have been collectively referred to as 'Sick Cloth Syndrome' and gave a troublesome feature that a new wear must be washed before putting it on[3]. Especially in the textile industry, various dyes and preparations are used in several processes such as pretreatment, dyeing and post processing. Although these processes are necessary for chromogenic feature and color fastness, it is a current trend to be concerned about effects on environment and human body. Especially, it was known that the dyeing process generates more waste water than other processes and several hundred thousand tons of dyeing sludge is generated. On top of that, metal dyes are mainly used in dyeing wool fabrics. Considering contamination and lethal damage to the environment and the human body by waste water including the heavy metal substances of the metal dyes, it is also important to improve treatment facilities for them. It is crucial that this is preceded by selecting eco-friendly dyes alternating the metal dyes above everything. From the starting point of the dyes, all process including dyeing and waste water disposal must be made eco-friendly gradually. The trend towards healthier lifestyles in these years will be continued in future and must be emphasized in all fields. Therefore, it is a task to advance to a future-oriented industry reflecting the trend in textile and dye industry[4-10].

In this study, we suggest a possibility of wool reactive dyes as one of the future-oriented dyes by dyeing 100% wool fabrics with traditional metallic acid dyes and wool reactive dyes, assessing their chromogenic features and color fastness and analyzing, comparing and assessing their heavy metal and harmful amine degree.

II. Experimental

1. Fabric sample and dye stuff

The sample used in this study was standard white wool fabric, which showed characteristics of fabric<Table 1>.

Four colors (Yellow, Red, Blue, Black) of wool reactive dyes developed in Korea and wool reactive dyes developed in a foreign country to substitute traditional metallic acid dyes. The other four colors (Yellow, Red, Blue, Black) of wool metallic acid dyes developed in Korea and wool reactive dyes developed in a foreign country to substitute traditional metallic acid dyes. Dyeing waste water from using the four color dyes of both domestic and foreign was compared, evaluated and analyzed.

2. Harmful amine analysis

The harmful amines were measured and analyzed with 35 LMBG 82.02-1, 2, 3, 4 method using GC/MS (Agilent 5973N, U.S.A.). 20 % of all dyes used in the textile industry are azo dyes.

<Table 1> Information of fabric

Fabric	Type	Density	Weight	Thickness
Wool 100%	Plain woven	74×71/inch^2	97±5g/㎡	0.28±0.02㎜

<Table 2> List of wool reactive dyes

	Wool Reactive		Metallic acid	
	Dye stuff	Color	Dye stuff	Color
Domestic	K1	Yellow	KK1	Yellow
	K2	Red	KK2	Red
	K3	Blue	KK3	Blue
	K10	Black	KK4	Black
Foreign	F1	Yellow	FF1	Yellow
	F2	Red	FF2	Red
	F3	Blue	FF3	Navy Blue
	F8	Black	FF4	Black

<Table 3> List of 24 Aryl Amine

No	Aryl Amine	CAS No.
1	4-Aminodiphenyl	92-67-1
2	Benzidine	92-87-5
3	4-Chloro-o-toluidine	95-69-2
4	2-Naphthylamine	91-59-8
5	O-Aminoazotoluene	97-56-3
6	2-Amino-4-nitrotoluene	99-55-8
7	p-Chloroamiline	106-47-8
8	2,4-Diaminoanisole	615-05-4
9	4,4'-Diaminodiphenylmethane	101-77-9
10	3,3'-Dichlorobenzidine	91-94-1
11	3,3'-Dimethoxybenzidine	119-90-4
12	3,3'-Dimethylbenzidine	119-93-7
13	3,3'-Dimethyl-4,4'-diaminodiphenylmethane	838-88-0
14	p-Cresidine	120-71-8
15	4,4'-Methylene-bis-(2-chloroniline)	101-14-4
16	4,4'-Oxidianiline	101-80-4
17	4,4'-Thiodianiline	139-65-1
18	o-Toluidine	95-53-4
19	2,4-Toluylenediamine	95-80-7
20	2,4,5-Trimethylaniline	137-17-7
21	p-Aminoazobenzene	90-04-0
22	o-Anisidine	95-68-1
23	2,4-Xylidine	87-62-7
24	2,6-Xylidine	60-09-3

There are 140 types of azo dyes synthesized from aryl amine and it is known that 24 types of acid dyes, 76 types of direct dyes, 4 types of disperse dyes, and 2 types of basic dyes according to color index of dyes are commercialized. Particular azo dyes may be classified into 24 aromatic amines by reduction decomposition as shown in below <Table 3>. They cause carcinogenic, allergic, and toxic aromatic amine and then prohibit using.

3. Heavy metal analysis

Contents of 16 types heavy metal in the dyes were analyzed by ICP(ULTIMA II, Jovin Evon Ultima2/France) and measured after acid digestion using nitric acid under the regulations of ETAD.

4. Exhaustion rate(%) measurement

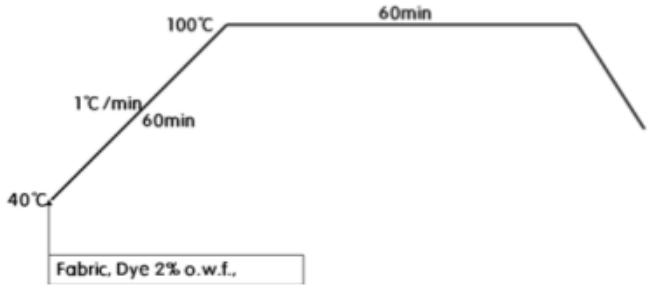
In order to understand dyeing behavior of the 8 types of dyes according to temperature and time, their exhaustion and half-dyeing time were measured using a dye behavior measuring equipment, Dye-o-meter. The dyeing curve measurement system be composed of a dyeing solution circulating machine and UV-visible ray spectrophotometer and measures their exhaustion change at maximum at the maximum absorption wavelength by phases during the dyeing process. As shown in the dyeing process of below <figure. 1>, 2% o.w.f dyeing solution was prepared with liquid ratio 1:20 at 40℃ using the Dye-o-meter, and then measured with 5 minutes of intervals during 120 minutes, adding it with a sample, raising the 1℃ temperature per min and maintaining the temperature at 100℃ for 60 minutes.

5. Color fastness to light

The color fastness to light was tested with Xenon Arc test method of ISO 150-B02. After exposing the test samples using Xenon weather-O-meter at 63℃ of temperature and 30% of humidity for 20 hours, color change of the test sample was compared with that of the reference blue fabric and its level was determined.

6. Color fastness to washing

The color fastness to washing was tested under the test method in ISO 105-C01. Six fibers(acetate, cotton, nylon, pet, acryl and wool) with 40×100㎜ in same size put them parallel and sew their shorter side, is attached to the test sample. The samples were washed with 5g/ℓ of soap solution using Launder-O-meter



<Figure. 1> procedure of dyeing to examine the exhaustion

in 1:50 of liquid ratio, at 40℃, for 30minutes.

7. Color fastness to rubbing

The color fastness to rubbing was tested for dry and humid condition under the test method in ISO 105-X12 (Crock Meter). Two test samples with 200×100㎜ of rectangular shape for each test condition types were prepared. The test samples for dry rubbing test and white cotton fabric for rubbing were incubated in dry condition at constant temperature and humidity for at least 4 hours and then were tested. The test samples for wet rubbing test and white cotton fabric for rubbing was made wet condition of 100% humidity with distilled water at room temperature prior to the test. Crock-O-meter loaded 900gd was covered with standard

<Table 4> Result of analysis harmful amine from domestic and foreign reactive dyes for wool

No	Aryl Amine	Concentration(㎎/㎏)							
		F1	F2	F3	F8	K1	K2	K3	K10
1	4-Aminodiphenyl	ND	ND	ND	ND	ND	ND	ND	ND
2	Benzidine	ND	ND	ND	ND	ND	ND	ND	ND
3	4-Chloro-o-toluidine	ND	ND	ND	ND	ND	ND	ND	ND
4	2-Naphthylamine	ND	ND	ND	ND	ND	ND	ND	ND
5	O-Aminoazotoluene	ND	ND	ND	ND	ND	ND	ND	ND
6	2-Amino-4-nitrotoluene	ND	ND	ND	ND	ND	ND	ND	ND
7	p-Chloroamiline	ND	ND	ND	ND	ND	ND	ND	ND
8	2,4-Diaminoanisole	ND	ND	ND	ND	ND	ND	ND	ND
9	4,4'-Diaminodiphenylmethane	ND	ND	ND	ND	ND	ND	ND	ND
10	3,3'-Dichlorobenzidine	ND	ND	ND	ND	ND	ND	ND	ND
11	3,3'-Dimethoxybenzidine	ND	ND	ND	ND	ND	ND	ND	ND
12	3,3'-Dimethylbenzidine	ND	ND	ND	ND	ND	ND	ND	ND
13	3,3'-Dimethyl-4,4'-diaminodi phenylmethane	ND	ND	ND	ND	ND	ND	ND	ND
14	p-Cresidine	ND	ND	ND	ND	ND	ND	ND	ND
15	4,4'-Methylene-bis-(2-chloroniline)	ND	ND	ND	ND	ND	ND	ND	ND
16	4,4'-Oxidianiline	ND	ND	ND	ND	ND	ND	ND	ND
17	4,4'-Thiodianiline	ND	ND	ND	ND	ND	ND	ND	ND
18	o-Toluidine	ND	ND	ND	ND	ND	ND	ND	ND
19	2,4-Toluylenediamine	ND	ND	ND	ND	ND	ND	ND	ND
20	2,4,5-Trimethylaniline	ND	ND	ND	ND	ND	ND	ND	ND
21	p-Aminoazobenzene	ND	ND	ND	ND	ND	ND	ND	ND
22	o-Anisidine	ND	ND	ND	ND	ND	ND	ND	ND
23	2,4-Xylidine	ND	ND	ND	ND	ND	ND	ND	ND
24	2,6-Xylidine	ND	ND	ND	ND	ND	ND	ND	ND

cotton fabric and made rub on the surface of test sample through 10 times of shuttle motion within 100mm for 10 second. Then, the contamination degree on the white cotton fabric was compared with the gray scale and its level was determined.

III. Result and Discussion

1. Results of harmful amine analysis

The harmful amine analysis resulted that as like the traditional 1:2 metal complex dyes, 24 types of harmful amines were not detected in total 8 types of wool reactive dyes including 4 foreign countries. The harmful amine analysis results types made in Korea and 4 types made in were displayed in below <Table 4>.

2. Results of heavy metal analysis

Comparing the wool reactive dyes with the traditional metal complex dyes, it was identified that contents of 16 type metal complex dyes in the reactive dyes were reduced significantly <Table 5-6>. It was found that heavy metals (Cr, Cu, Zn) were detected in only the black dye made in a foreign country, but their amount were small. It was also found that in the wool reactive dyes made in Korea, small amount of Cr were detected only in Yellow and Black and small amount of Cu was detected in Blue. In comparison with wool reactive dyes, metallic acid dyes contained many kinds of metal<Table 6>.

<Table 5> Result of analysis of containing heavy metal from domestic and foreign reactive dyes for wool

No	Heavy Metal	Concentration(㎎/㎏)							
	Metal	F1	F2	F3	F8	K1	K2	K3	K10
1	As	ND	ND	ND	ND	ND	ND	ND	ND
2	Hg	ND	ND	ND	ND	ND	ND	ND	ND
3	Se	ND	ND	ND	ND	ND	ND	ND	ND
4	Sb	ND	ND	ND	ND	ND	ND	ND	ND
5	Zn	ND	ND	ND	18	ND	ND	ND	ND
6	Pb	ND	ND	ND	ND	ND	ND	ND	ND
7	Ni	ND	ND	ND	ND	ND	ND	ND	ND
8	Cd	ND	ND	ND	ND	ND	ND	ND	ND
9	Co	ND	ND	ND	ND	ND	ND	ND	ND
10	Sn	ND	ND	ND	ND	ND	ND	ND	ND
11	Mn	ND	ND	ND	ND	ND	ND	ND	ND
12	Fe	ND	ND	ND	ND	ND	ND	ND	ND
13	Cr	ND	ND	ND	5	9.7	ND	ND	ND
14	Cu	13	ND	ND	13	ND	ND	12.9	ND
15	Ag	ND	ND	ND	ND	ND	ND	ND	ND
16	Ba	ND	ND	ND	ND	ND	ND	ND	ND

3. Results of Exhaustion rate(%)

It was found that the exhaustion rate of wool reactive dyes made in foreign countries was higher as much as 1%, they shows similarly high tendency. For the half-dyeing time, It was found that there was a significant difference between domestic and foreign products in the Black and Yellow dye. The half-dyeing time and exhaustion rate of dyes were showed in below <Table 7> and the exhaustion rate of each dye were shown in Fig.2-3. In comparison with wool reactive dyes, the exhaustion rate of metallic acid dyes was more higher than wool reactive dyes<Table 8>.

<Table 6> Result of analysis of containing heavy metal from domestic and foreign metallic acid dyes

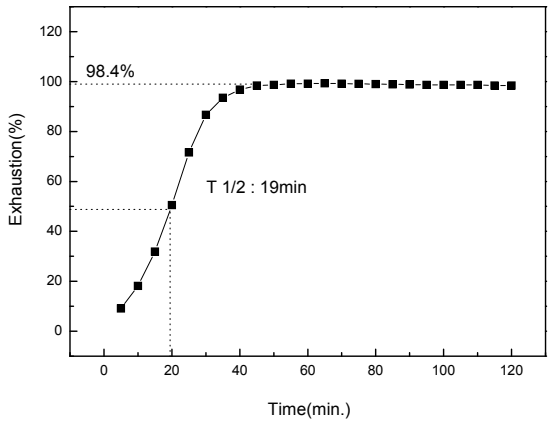
No	Heavy Metal	Concentration(㎎/㎏)							
	Metal	FF1	FF2	FF3	FF4	KK1	KK2	KK3	KK4
1	As	ND	ND	ND	ND	ND	ND	ND	ND
2	Hg	ND	ND	ND	ND	ND	ND	ND	ND
3	Se	ND	ND	ND	ND	ND	ND	ND	ND
4	Sb	ND	ND	352.8	1921.2	ND	ND	118.6	38.0
5	Zn	ND	ND	ND	ND	ND	ND	ND	66.0
6	Pb	ND	ND	ND	ND	ND	ND	ND	ND
7	Ni	46.7	ND	19.7	21.0	414.0	36.4	35.9	ND
8	Cd	ND	ND	ND	ND	ND	ND	ND	ND
9	Co	81.8	177.0	222.1	157.7	507.9	471.8	439.1	ND
10	Sn	ND	ND	ND	ND	ND	ND	ND	ND
11	Mn	85.7	24.6	13.5	22.0	531.0	42.1	37.8	ND
12	Fe	64.4	160.6	217.5	137.3	371.3	426.3	400.3	156.0
13	Cr	12161.3	21704.5	14538.2	21164	ND	20938.3	21089.2	90763
14	Cu	ND	ND	35.0	50.4	37.2	ND	ND	72.0
15	Ag	ND	25.1	ND	ND	87.7	ND	ND	ND
16	Ba	ND	51.8	70.2	60.6	36.0	43.0	30.0	86.0

<Table 7> $T_{1/2}$ and Exhaustion rate of domestic and Foreign reactive dyes for wool

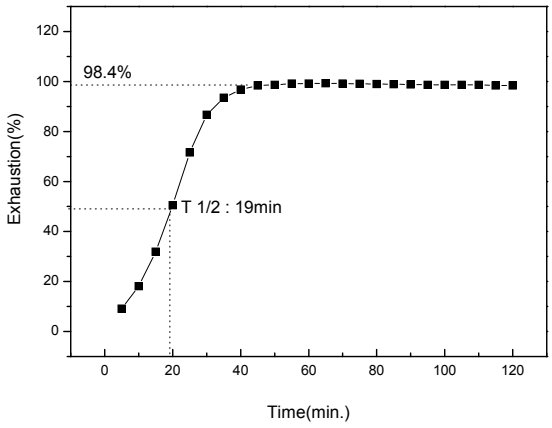
No	Type		Dye Stuff	$T_{1/2}$(min)	Exhaustion(%)
1	Domestic	K1	Yellow	19	98.4
2		K2	Red	19	98.4
3		K3	Blue	21	98.8
4		K10	Black	31	99.9
5	Foreign	F1	Yellow	8	98.4
6		F2	Red	23	99.0
7		F3	Blue	21	99.9
8		F8	Black	26	100

<Table 8> $T_{1/2}$ and Exhaustion rate of domestic and Foreign metallic acid dyes for wool

No	Type		Dye Stuff	$T_{1/2}$(min)	Exhaustion(%)
1	Domestic	KK1	Yellow	41	99.9
2		KK2	Red	39	99.8
3		KK3	Blue	47	97.9
4		KK4	Black	54	94.1
5	Foreign	FF1	Yellow	29	99.9
6		FF2	Red	48	97.3
7		FF3	Navy Blue	34	99.2
8		FF4	Black	44	99

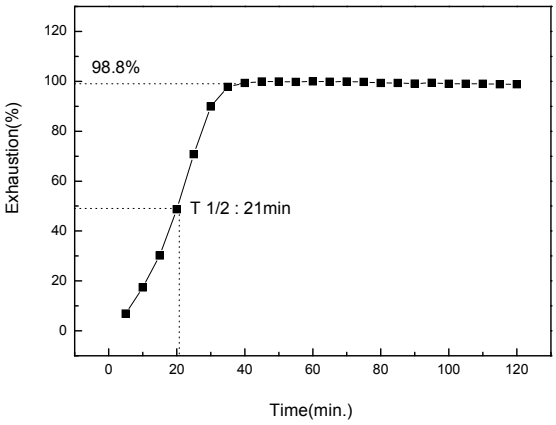


K1(Yellow)

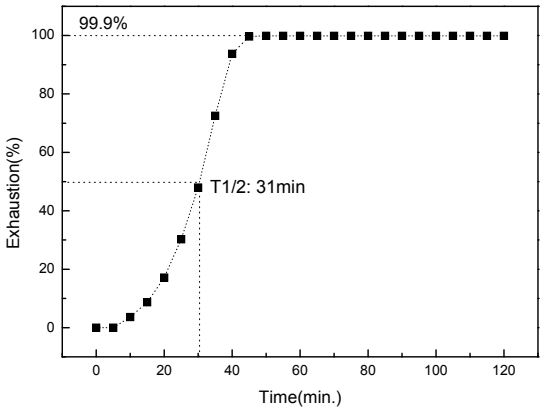


K2(Red)

<Figure. 2> Exhaustion rate curves of domestic wool reactive dyes

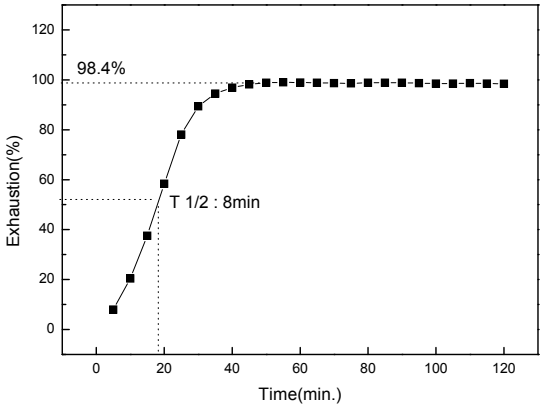


K3(Blue)



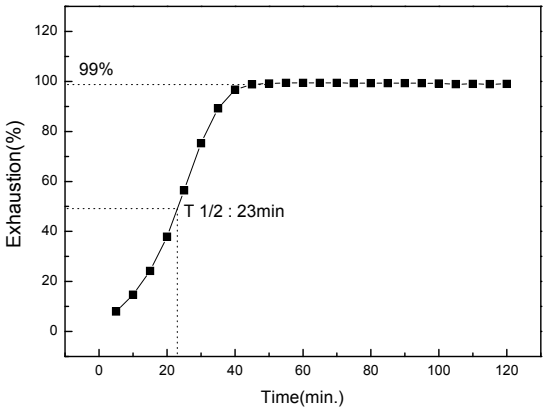
K10(Black)

<Figure. 2> Continued

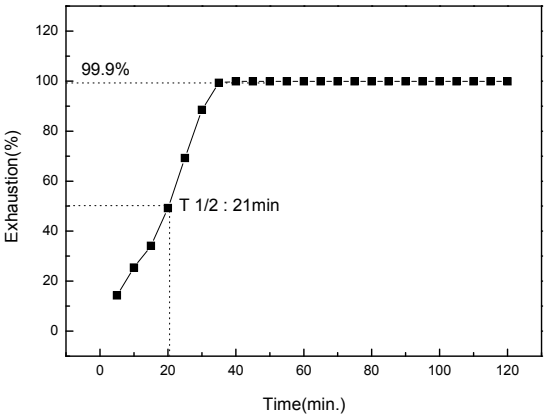


F1(Yellow)

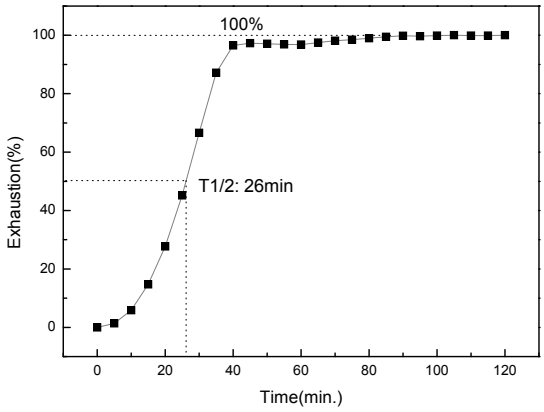
<Figure. 3> Exhaustion rate curves of foreign wool reactive dyes



F2(Red)



F3(Blue)



F8(Black)

<Figure. 3> Continued

4. Results of color fastness

The color fastness test results with each dye were showed in <Table 8>.

For the color fastness to light, it was found that it was excellent in both domestic and foreign dye products.

The foreign Black dye was better as much as 1 class than domestic Black dye. It was found that the color fastness to washing was different in only Black dye. It was suggested that the Black domestic dye had a possibility of migration to the acetate and wool fabric.

It was found that the color fastness to rubbing was measured to be excellent high. All of the domestic and foreign dye products in the color fastness to rubbing test were examined in the 4-5 grade.

Ⅳ. Conclusion

Wool fabric was dyed by four types of currently commercialized foreign wool reactive dyes and four types of domestic wool reactive dyes developed for minimizing environmental pollution such as waste water and sludge. Their chromogenic feature, heavy metal content and were assessed. The following conclusions are made;

1. It was found in hazard test in dye itself that 24 types of harmful amines were not detected in both foreign and domestic wool reactive dye products. However, it was identified that it was required to add hazard assessment test in dyeing waste water.

2. The heavy metal analysis resulted that heavy metals were detected hardly in both foreign and domestic products. It was found for detected heavy metals that in case of Yellow dye, Cu was detected in the foreign product and Cr was detected in the domestic product. Zn, Cr, and Cu were detected in the foreign Black dye and Cu was detected in the domestic Blue dye. In the domestic Black dye and the foreign Blue dye, no heavy metal was detected.

3. Wool fabric which was dyed by metallic acid dyes was highly strong and exhausted rate than wool dyed by wool reactive dyes because metallic acid dyes contained various kinds of metal. The exhaustion was high similarly in both reactive dyes and metallic acid dyes. Because the foreign Yellow dye has remarkably shorter

<Table 9> Result of Colorfastness

No.	Dye stuff	Color fastness to Light	Colorfastness to Washing						Colorfastness to Rubbing	
			Acetate	Cotton	Nylon	PET	Acryl	Wool	Dry	Wet
1	K1	5-6	4-5	4-5	4-5	4-5	4-5	4	5	4-5
2	K2	5-6	4-5	4-5	4-5	4-5	4-5	4	5	4
3	K3	4-5	4-5	4-5	4-5	4-5	4-5	4	5	4
4	K10	4	5	5	4-5	5	5	4	5	4-5
5	F1	5-6	4-5	4-5	5	4-5	4-5	4	5	4-5
6	F2	5-6	4-5	4-5	4	4-5	4-5	4	5	4
7	F3	4-5	4-5	4-5	4-5	4-5	4-5	4	5	4
8	F8	5-6	4-5	5	4-5	5	5	4-5	5	4

dyeing time than other dyes, it may cause unlevel dyeing.

4. It was found that the color fastness was excellent generally in both domestic and foreign reactive dyes for wool. For color fastness to washing, it was found that only domestic Black dye product has lower grade than foreign products. The reason is that its heavy metal content is smaller than that of foreign products.

5. The metal acid dyes generally used in dyeing wool fabric contain large amount of heavy metals and harmful amines. It is evaluated that they should be gradually converted into the reactive dyes for wool.

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