Journal of Fashion Business
Vol. 9, No. 3, pp.114~124(2005)

Effects of Mordanting, Dyeing, Rinsing, and Fiber Characteristics on the Air-permeability and Color of Fabrics Dyed using Cochineal Dyestuff

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Abstract

Based on the previous study, three types of synthetic fibers comprising nylon, PET, and acrylic fibers were investigated in this study. The effect of mordanting on the air-permeability and dyeing properties of fabrics was investigated. The effect of rinsing process on the air-permeability and color was quantitatively investigated by rinsing the mordanted fabric specimens 1~3 times after mordanting. The air-permeability changed peculiarly according to the characteristics of the fiber materials after mordanting. The air-permeability values of nylon and acrylic fabric specimens dropped significantly after mordanting. On the other hand, those of PET fabric specimens hardly changed after mordanting. The metal ions absorbed on the fibers of nylon and acrylic fabrics did not show the mordanting effect. Regardless of mordanting, cochineal dyestuff made direct links with the molecular chains in nylon fabrics exhibiting dark colors. After dyeing acrylic fabrics, the color did not develop at all, even though partial components of the cochineal dyestuff were absorbed apparently.

Key words : nylon, PET, acrylic, mordant, air-permeability

I. Introduction

In the previous study[1], the air-permeability changes were investigated after mordanting cotton, nylon, PET, acrylic, and silk fibers using mordants. In addition, the air-permeability of cotton and silk fibers were investigated after dyeing using cochineal. The air-permeability values decreased generally after mordanting[2] with minor differences according to fiber materials

and mordant types. This explains that the air-permeability drops when the metal ions are absorbed on the fibers. There are many functional sites, which are able to form coordinate bonds with metal ions, inside the molecular chains of cotton and silk fibers. It was conjectured that the air-permeability decreased substantially after mordanting since the functional sites formed coordinate bond with the metal ions.

Absorption ability of the nylon fiber molecule is not high due to its high crystallinity even if there are functional sites in the nylon fiber—a synthetic fiber. The metal ions are not absorbed on the PET fiber since its crystallinity is very high and functional sites are almost nil. As a result, PET fabric specimens did not show any change in the air-permeability after mordanting. On the other hand, due to the presence of —COOH groups, the metal ions were absorbed in quantity on acrylic fibers, and the air-permeability decreased significantly after mordanting.

In the previous study, the color and air-permeability after dyeing were investigated only for cotton and silk fibers. In this study, as a continuing study, the changes in the air-permeability and the color changes of nylon, PET, and acrylic fibers, among synthetic fibers, were investigated after dyeing using cochineal.

II. Experiments

1. Fabrics and chemicals

1) Fabrics for dyeing

The specimens used in this study are polyester, acrylic, and nylon standard fabrics conforming to the specifications of KS S 0905, purchased from the KATRI.

2) Dyestuff

Commercially available cochineal powder (Mikwang Fine Chemical, Korea) was used.

3) Mordants

Mordants used in this study were Cu, Sn, Al, Fe, and Cr compounds equivalent to the grades of reagent grade 1 or extra pure reagents.

- Cupric sulfate pentahydrate : $CuSO_4 \cdot 5H_2O$
- Stannous chloride : $SnCl_2 \cdot 2H_2O$
- Aluminum potassium sulfate : $AlK(SO4)_2 \cdot 12H_2O$
- Ferric chloride, hexahydrate : $FeCl_3 \cdot 6H_2O$
- Chromium(Ⅲ) nitrate enneahydrate : $Cr(NO_3)_3 \cdot 9H_2O$

2. Dyeing methods

1) Mordanting process

The concentration percentages of the mordants were adjusted to be 2%, 2%, 2%, 2%, and 5% for the Cu, Sn, Fe, Cr, and Al, respectively. The liquor ratio was set to 1:100 for the mordanting liquor bath. As the temperature of the mordanting liquor reached 40℃, the fabric specimens were immersed in the mordanting bath, then the bath temperature was raised to 60℃, and subsequent mordanting was maintained for 40 minutes. The mordanted fabrics were air-dried in the lab.

In order to observe the change according to the number of rinsing operations, six fabric

specimens were mordanted and air-dried first. Out of six mordanted specimens, two were used for direct dyeing without rinsing, two were rinsed once, and the remaining two specimens were twice for the subsequent dyeing.

2) Dyeing process

Concentration of 2% was selected for the cochineal dyeing, and the liquor ratio was set to 1:100.

As the dye bath temperature was raised to 40℃, the mordanted cotton and silk fabric specimens using Cu, Sn, Al were immersed in the dye bath, then the bath temperature was raised to 60℃, and subsequent dyeing was maintained for 60 minutes. After the dyeing, specimens were not rinsed immediately, but remained in the lab for air-drying almost a day, and then rinsed and dried.

3) Air-permeability test

Air-permeability tester (Model FX3300, Textest, Switzerland) was used to measure the air-permeability of the fabric specimens at the specified range of 7. The number of the measurement replications were 3, and the readings were averaged.

4) Color measurement

A colorimeter (Model CR-100b, Minolta, Japan) was used to measure L^*, a^*, b^* of the treated fabrics and ΔE values were calculated based on the corresponding control fabrics.

III. Results and Discussion

1. Fabrics and chemicals

As a reference, the changes of air-permeability after mordanting of nylon, PET, and acrylic fibers were presented in 〈Table 1〉. An outline of the 〈Table 1〉 was already discussed in the Introduction.

As shown in 〈Table 1〉, the air-permeability values were centered around 27.0 for the nylon fabric specimens after mordanting, regardless of the mordant types. In 〈Table 2〉, the air-permeability values of the fabrics dyed using cochineal were presented. After dyeing of unmordanted nylon fabric, the air-permeability of the nylon was 29.0. This demonstrates that the air-permeability was decreased even when the cochineal dyestuff was directly taken up by the nylon under unmordanted state. As shown in 〈Table 2〉, mordanted dyeing of nylon decreased the air-permeability values by 2~3 compared to the unmordanted case. In the end, the air-permeability values of the mordanted dyeing case and the mordanting only case in the case of nylon fabric specimens coincided exactly. This phenomenon provokes the following questions :

" What are the reasons of coinciding air-permeability values of the mordanting only case and the mordanted dyeing case in nylon fabrics? "

〈Table 1〉 Change of air-permeability according to the number of rinsings after the mordanting process

Application of Mordanting	Mordants	Number of rinsings after mordanting	Air-permeability ($cm^3/cm^2/s$)		
			Nylon	PET	Acrylic
Unmordanted	–	–	36.6	14.6	101
Mordant	$CuSO_4$	0 (After mordant)	26.9	15.1	59.1
		1	25.6	16.9	59.5
		2	27.0	17.2	61.5
	$SnCl_2$	0 (After mordant)	27.6	16.1	61.7
		1	27.4	16.6	59.5
		2	28.6	16.6	64.4
	$AlK(SO_4)_2$	0 (After mordant)	26.3	15.8	64.9
		1	28.3	15.5	79.7
		2	27.6	15.2	72.4
	$FeCl_3$	0 (After mordant)	27.5	14.3	75.9
		1	27.0	15.2	66.7
		2	23.6	15.6	77.4
	$Cr(NO_3)_3$	0 (After mordant)	26.5	16.2	67.5
		1	26.7	15.0	77.1
		2	27.0	14.9	70.5

When we reviewed the previous studies, we found that, in general, the air-permeability values differed from each other in the cases when the mordanting was introduced separately and when the dyeing and the mordanting were introduced together. As shown in the previous study,[1] the cotton fiber and silk fiber have shown different air-permeability values in the case of mordanting only and in the case of mordanted dyeing. However, in nylon, this tendency did not hold. This phenomenon suggests that the coordinate bond was not formed between metal ions and dyestuffs in nylon. In other words, even though the dyestuff molecules were introduced to the nylon molecular chains with the metal ions absorbed by the mordanting, coordinate bond complexes were not formed. It is clear that the dyestuff did not make bond with the metal ions but made bonds directly with the nylon molecular chains.

The peculiarities shown in nylon dyeing behavior would be verified if the following experimental results might suffice two assumptions below :

① If dyeing is implemented without any problems under unmordanted state, the cochineal dyestuff will be bonded to the nylon molecular chains directly without the aid of mordants.

② If the same color is developed regardless of the metal ion types, furthermore, the cochineal dyestuff will be bonded to the nylon molecular chains regardless of the mordanting.

The assumptions will be dealt with in detail in the color analysis of dyed fabrics section later. The air-permeability values were maintained constantly regardless of the number of rinsings after mordanting except for the Fe mordanting.

〈Table 2〉 Air-permeability of cochineal dyed fabrics: nylon, PET and acrylic

Application of Mordanting	Mordant	Number of rinsings after mordanting	Fabric		
			Nylon	PET	Acrylic
Unmordanted	control (grey)	–	36.6	14.6	101.0
	dyed fabric	–	29.0	14.8	50.8
Mordant	$CuSO_4$	0(After Mordant)	26.6	15.6	58.8
		1	25.6	17.5	56.5
		2	26.7	17.5	53.3
	$SnCl_2$	0(After Mordant)	27.9	15.7	55.1
		1	27.5	16.3	55.3
		2	27.8	16.1	56.0
	$AlK(SO_4)_2$	0(After Mordant)	26.1	15.3	64.5
		1	28.2	15.5	76.5
		2	26.9	15.2	65.2
	$FeCl_3$	0(After Mordant)	27.5	14.3	77.2
		1	25.7	15.5	65.9
		2	23.6	15.7	75.2
	$Cr(NO_3)_3$	0(After Mordant)	26.0	15.7	66.9
		1	26.2	14.5	65.2
		2	26.1	14.9	67.8

Next, the air-permeability values of PET fabric specimens have shown almost similar tendency to those of nylon fabric specimens. The air-permeability values were almost the same for the case of the mordanting only and the case of mordanted dyeing.

However, the air-permeability values of the unmordanted dyeing case of PET differed from those of nylon. In the unmordanted dyeing, the air-permeability of nylon decreased while that of PET did not. From this, it was inferred that dye uptake was not accomplished at all in the unmordanted case. In view of various physical and chemical characteristics of PET fibers, the possibility of accomplishing the dyestuff absorption both in the unmordanted and in the mordanted cases is very slim. It was confirmed that the air-permeability decreased in case the metal ions were absorbed in the fiber molecular chains by mordanting process, based on the comparison of the PET and nylon air-permeability values. It became clear that the air-permeability decreased in case the dye molecules were directly absorbed by the fiber molecular chains.

Next, acrylic fibers will be reviewed. The air-permeability values of acrylic fibers decreased more in the case of dyeing than in the case of mordanting only.

As shown in 〈Table 1〉, the air-permeability value was maintained more than 60 after mordanting. After the unmordanted dyeing procedure, the air-permeability value decreased down to 50 or so. Especially in Sn mordanting, the decrease of the air-permeability was significant after dyeing. Unlike in the case of PET, the air-permeability in the case of acrylic fibers decreased significantly. It is presumed that the reason for this is related to the functional sites in the molecular structures.

2. Color changes according to cochineal dyeing

〈Table 3〉 presents the color measurement results of dyed nylon fabric specimens. Regardless of the mordant types, △E values were maintained in the range of 65~66. The peculiar dyeing mechanism of nylon was explained by the fact that △E differences were almost nil between the unmordanted case and the mordanted case. The assumptions established in the previous nylon air-permeability discussion section were elucidated here.

That is, in nylon, regardless of the types of mordants or the mordanting treatment, since almost the same color was developed, the mordanting effect is negligible. Coordinate bond complex formed by metal ions and dyestuffs were not present even if the metal ions were absorbed by the nylon due to mordanting.

The fact that the amount of air-permeability decrease was almost the same explains the following characteristics of dyeing :

> " Cochineal dyestuff molecules are taken up directly by the nylon molecular chains without forming coordinate bonds with the metal ions. "

In spite of the high crystallinity of the nylon, direct dye uptake was accomplished by the functional groups such as $-NH_2$ or $-COOH$ end groups in the nylon molecules.

Especially, it is presumed that the $-NH_2$ plays a big role toward the cochineal, which is an acid dyestuff. Except for the Fe mordanting, a^*, b^* values increased, though minimal, along with △E values compared to the unmordanted case.

〈Table 3〉 Color measurement of nylon fabric specimens

Application of Mordanting	Mordant	number of rinsings after mordanting	Color Difference			
			L^*	a^*	b^*	△E
Unmordanted	control (grey)	–	87.1	−0.9	0.1	–
	dyed fabric	–	37.6	37.7	15.1	64.56
Mordant	$CuSO_4$	0(After Mordant)	36.9	38.0	15.0	65.20
		1	37.0	38.0	15.2	65.22
		2	36.8	38.4	15.8	65.72
	$SnCl_2$	0(After Mordant)	38.2	39.2	18.9	66.02
		1	38.2	39.0	18.5	65.74
		2	38.3	38.8	18.4	65.51
	$AlK(SO_4)_2$	0(After Mordant)	38.1	39.4	18.7	66.13
		1	38.6	39.4	18.9	65.80
		2	38.5	39.4	19.1	65.92
	$FeCl_3$	0(After Mordant)	36.9	34.9	16.9	63.90
		1	37.0	34.9	17.4	63.95
		2	37.4	34.9	17.1	63.57
	$Cr(NO_3)_3$	0(After Mordant)	37.5	37.7	18.9	65.57
		1	37.5	37.8	19.1	65.68
		2	37.6	37.6	18.9	65.47

This suggests that fine color change is caused by the mordanting. Since the amount of increase in b^* values is significant, the color shifted strongly toward yellow. It is a very exceptional phenomenon that nylon, a synthetic fiber, is readily dyed by the natural dyestuff without the mordant treatment.

〈Table 4〉 shows the color changes of PET fibers. As expected, PET was not dyed at all in the unmordanted case. The value of △E 0.66 meant impossibility of dyeing. Even if the values of △E range 13∼14 were maintained in Sn and Fe mordanting, this is not more than numbers.

In actual dyed fabric specimens, the color development was quite negligible from a practical point of view. The fact that PET fiber molecules do not have any functional groups, and are highly crystalline makes the PET inactive with the metal ions or dye molecules. 〈Table 4〉 clearly demonstrates the above explanation.

〈Table 4〉 Color measurement of PET fabric specimens

Application of Mordanting	Mordant	number of rinsings after mordanting	Color Difference			
			L^*	a^*	b^*	△E
Unmordanted	control (grey)	–	90.2	−0.8	−0.3	
	dyed fabric	–	89.6	−0.6	−0.2	0.66
Mordant	$CuSO_4$	0(After Mordant)	89.3	−0.4	0.2	1.07
		1	89.4	−0.4	0.1	1.03
		2	89.3	−0.4	0.0	1.02
	$SnCl_2$	0(After Mordant)	83.1	11.4	2.3	14.37
		1	83.2	11.0	2.3	13.99
		2	83.1	11.0	2.2	13.99
	$AlK(SO_4)_2$	0(After Mordant)	88.8	0.6	0.0	2.04
		1	89.3	0.6	0.0	1.71
		2	88.9	1.0	0.0	2.27
	$FeCl_3$	0(After Mordant)	81.9	3.3	9.6	13.52
		1	81.6	3.5	9.3	13.62
		2	81.6	3.6	8.7	13.20
	$Cr(NO_3)_3$	0(After Mordant)	85.9	3.4	2.8	6.72
		1	86.4	3.1	2.4	6.05
		2	85.9	3.8	2.5	6.87

〈Table 5〉 shows the color changes of acrylic fibers. Unlike PET fiber case, air-permeability values had decreased significantly in the case of acrylic fibers. This decrease after mordanting implies that metal ions were absorbed in the acrylic fiber molecular chains. The air-permeability decrease in the case of unmordanted dyeing also implies the dye molecules were absorbed in the acrylic fiber molecular chains. However, in 〈Table 5〉, on examining color measurement results, we were confronted with unexpected values. Except for the Sn and Fe mordanting, there was almost no color development based on the △E values in the table. On top of that, dyeing is not accomplished even in the unmordanted dyeing case. It is inferred that the mordanting effect did not develop even if the metal ions were absorbed in the acrylic fiber molecular chains. The absorbed metal ions did not form coordinate bonds with the color components capable of exhibiting their inherent colors.

〈Table 5〉 Color measurement of acrylic fabric specimens

Application of Mordanting	Mordant	number of rinsings after mordanting	Color Difference			
			L^*	a^*	b^*	△E
Unmordanted	control (grey)	–	90.9	−2.5	4.1	–
	dyed fabric	–	90.4	1.1	3.0	1.90
Mordant	$CuSO_4$	0(After Mordant)	87.6	0.7	1.7	5.17
		1	87.9	0.8	1.4	5.22
		2	88.4	0.3	2.2	4.25
	$SnCl_2$	0(After Mordant)	82.3	12.4	4.7	17.23
		1	82.7	12.2	4.7	16.85
		2	82.0	12.8	4.6	17.72
	$AlK(SO_4)_2$	0(After Mordant)	85.6	4.1	0.5	9.14
		1	85.8	3.7	1.1	8.53
		2	86.2	3.3	1.0	8.12
	$FeCl_3$	0(After Mordant)	78.0	4.6	10.8	16.17
		1	76.6	5.1	10.9	17.55
		2	77.2	4.9	10.8	16.96
	$Cr(NO_3)_3$	0(After Mordant)	85.5	3.8	4.8	8.37
		1	85.6	3.6	4.7	8.11
		2	85.8	3.5	4.4	7.88

In the unmordanted dyeing, irrespective of the decrease in air-permeability of acrylic fabrics, color did not develop. This phenomenon explains that the color components capable of developing colors among cochineal dye are not absorbed.

There have been several cases of experimental results in which colors were not developed even if the color components were absorbed after the completion of dyeing process.[3)]

It is clear that specific color components comprising cochineal dye could not develop colors even if absorbed.

IV. Conclusions

As one of the series, nylon, PET, and acrylic synthetic fibers were employed in this study. The effects of mordanting of these synthetic fibers on the air-permeability and dyeing were investigated. The effect of rinsing process on the air-permeability and color was quantitatively investigated by rinsing the mordanted fabric specimens 1~3 times after mordanting. It has been known that the air-permeability decreased when the mordants were absorbed in polymeric

fibers, based on existing studies. The change in air-permeability by mordanting has become a measure discerning the mordanting effect. In this study, in order to verify the detachment of metal ions remaining on the fiber surface after mordanting, the mordanted fabrics were rinsed 1~3 times. The following conclusions were obtained through interpretations by associating the air-permeability changes and colors according to the mordanting and dyeing.

1. The air-permeability changed peculiarly according to the characteristics of fiber materials after mordanting. The air-permeability values of nylon and acrylic fibers significantly decreased after mordanting. Those of PET fibers hardly changed after mordanting.

2. It was estimated that the decrease of air-permeability values of nylon and acrylic fibers, in which functional groups, capable of absorbing metal ions, were present in the molecules, was due to the absorption of mordants. On the other hand, PET did not absorb mordants due to the high crystallinity and to the absence of functional groups.

3. The change of air-permeability was negligible even with the repeated rinsing cycles up to 3 times. It was interpreted that the metal absorption on the fiber surface was not excessive.

4. The air-permeability decreased even if the cochineal dyestuffs were absorbed in the fiber molecular chains by the unmordanted dyeing. The decrease of air-permeability values were significant in nylon and acrylic fibers after the unmordanted dyeing. On the other hand, dye uptake was not accomplished in PET fibers. Air-permeability change was almost nil.

5. In nylon fibers, the metal ions absorbed in the fiber did not show mordanting effect. In nylon fibers, the nylon molecules were dyed by cochineal dyestuffs exhibiting dark color regardless of mordanting.

6. Also in acrylic fibers, he metal ions absorbed in the fiber did not show mordanting effect. In acrylic fibers, the color was not developed after dyeing even if the fiber molecules were certainly dyed by some of the cochineal components.

References

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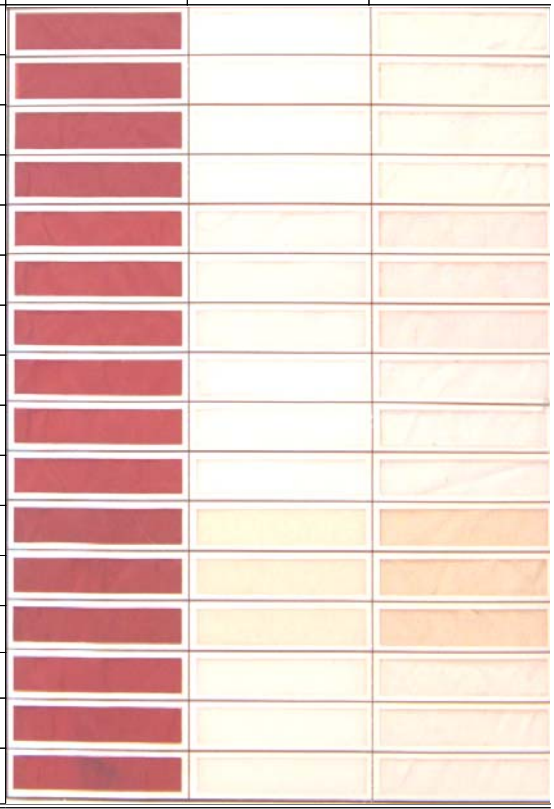
Received 1 April 2005, Accepted 3 June 2005.

Appendix. Dyed fabric specimens using cochineal after mordanting, nylon, PET, and acrylic.

Application of Mordant	Mordant	Number of rinsings after mordanting	Fabric		
			Nylon	PET	Acrylic
Unmordanted	dyed fabric	–			
Mordanted	$CuSO_4$	0(After Mordant)			
		1			
		2			
	$SnCl_2$	0(After Mordant)			
		1			
		2			
	$AlK(SO_4)_2$	0(After Mordant)			
		1			
		2			
	$FeCl_3$	0(After Mordant)			
		1			
		2			
	$Cr(NO_3)_3$	0(After Mordant)			
		1			
		2			