Journal of Fashion Business
Vol. 8, No. 6, pp.137~145(2004)

Effect of Rinsing after Mordanting on the Air-permeability and Dyeing of Fabrics with Cochineal Dyestuff

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Abstract

According to the experimental results, it has been reported by several researchers that the air-permeability values of the fabrics mostly decreased by the mordanting during the dyeing procedure. The exact quantitative information, however, has not been presented so far. In this study, the change of the fabric air-permeability was investigated quantitatively. At the same time, the change of the fabric air-permeability according to the dyeing procedure. In order to investigate the possibility of the detachment of the metal ions on the fiber or fabric surface, the change of the air-permeability was investigated after several rinsing of the mordanted fabrics. By comparing the color differences of the cochineal dyed fabrics which were subjected to rinsing procedure after mordanting, the effect of the rinsing of the mordanted fabrics on the dyeing of fabrics was investigated. At the range of mordant concentration, 2% Cu, 2% Sn, 2% Fe, 2% Cr, 5% Al, the metal ions are not excessively absorbed on the fiber surface. Also, any remarkable detachment of the metal ions does not accompany after the mordanting with the subsequent rinsing procedure.

Key words: Mordant, Rinsing, Cochineal, Air-permeability

I. Introduction

Mercury, tin, zinc, etc. have been commonly used as the antimicrobial finishing agents in the textile industry. in general. However, the use of heavy metals has been banned due to the fatal toxicity of the heavy metals for ten or more years. Despite the safety measure, such heavy metals are being employed without any precaution in many natural dyeing processes. From the view point that the heavy metals used in the antimicrobial finishing and those in the natural dyeing practices offer the same degree of toxicity to the health and the environment, the safety involved in the mordanting processes in the natural dyeing practices should be thoroughly taken into consideration.

In the antimicrobial finishing, the heavy metals are adhered on the surface of textile fibers, in other words, they remain on the fiber to reveal the antimicrobial function with the concentration on the fiber reaching several ppm's. The absolute level from the point of view of the MIC to reduce the microorganisms is quite low; the hazardousness of the level is, however, questionable.

The use of mordanting agent is mistakenly regarded as being also environmentally safe under the over-simplified notion that since the colorants for natural dyeing process are environmentally safe that additional materials for the process are also safe. It has been confirmed that the amount of required mordants added in the natural dyeing process far exceeds that for the antimicrobial processes. For instance, while the concentration of the metal ion solution for the antimicrobial finishing is usually around several ppm level, that for the natural dyeing reaches several percent level. We often find that the concentration of the metal ion solution exceeds 10~20%.

The metal ion solutions are mostly discharged as dyeing effluents after the dyeing process is over. It is, however, hard to disregard the possibility that the metals may remain on the fiber surface as highly concentrated. It is, as a consequence, of prime importance that the addition of the mordant should be minimized unless there is adverse effect in the dyeing process.[1,2)]

It is deduced that the air-permeability decreases as the metallic ions are adsorbed on the surface of fiber during the mordanting process.[3)] Based on this fact, the phenomenon of air-permeability reduction is concluded as supplying the information regarding the remaining metal ions on the fiber surface.

In this study, if there remained excessive amount of metal ion on the fiber surface, it is postulated to possibly remove the excessive amount of metal ion by rinsing the mordanted fabric several times. It has been known that the fiber itself has the ability to form coordinate bonds to the metal ions with less degree than the ability of ion-exchange resins or that of chelate resins. In this study, the degree of desorption of the metal ions was estimated by rinsing the mordanted fabrics several times using de-ionized water. The effect of rinsing on the dyeing was also quantitatively investigated.

II. Experiment

1. Fabrics and chemicals

1) Fabrics for dyeing

The specimens used in this study are cotton, silk, 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 : $Alk(SO_4)_2 \cdot 12H_2O$
- Ferric chloride, hexahydrate : $FeCl_3 \cdot 6H_2O$
- Chromium(III) nitrate enneahydrate : $Cr(NO_3)_3 \cdot 9H_2O$

2. Dyeing methods and test

1) Mordanting process

The concentration percentages of the mordants were adjusted to be 2% Cu, 2% Sn, 2% Fe, 2% Cr, and 5% Al, respectively. The liquor ratio was set to 1:100 for the mordanting liquor bath. As the temperature of the mordanting liquor reached 40˚C, the fabric specimens were immersed in the mordanting bath, then the bath temperature was raised to 60˚C, 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˚C, 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˚C, 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

Textest FX 3300 Air-permeability tester(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 (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

<Table 1> shows the air-permeability change for the mordanted cotton, nylon, PET, acrylic, and silk fabric specimens using Cu, Sn, Al, Fe, and Cr. The air-permeability generally decreased, even though there are some differences due to the fiber composition types and mordant types.

In the case of cotton fabric specimens, Cu- and Sn-mordanted fabrics showed decrease of air-permeability value of 15 compared to the Al-, Fe-, and Cr-mordanted fabrics. It seems to be a natural consequence considering the absorption ability of cotton for the metal ions. It has been known that cotton fibers have the -OH end groups in the molecular structure, which govern the most of the chemical reactions of the fiber. Hydroxyl groups have medium level reactivity. It is known that while these show high absorption capability toward Cu and Sn, the capability toward Al, Fe, and Cr are low. It showed as a summation that the air-permeability of the treated cotton fabrics decreased much greater if the amount of the absorption of the metal ion toward cotton fibers increased.

In the case of nylon fabric specimens, the air-permeability values decreased about 10 regardless of the types of the mordanting agents after the mordanting. It is known that there are -NH^2 end groups, i. e. amine end groups, in the nylon molecular structure in small amount that is capable of forming coordinate bonds with the metal ions. However, it is expected that the metal ion absorption capability of the nylon compared to the cotton fibers is low, since the nylon fibers are highly crystalline and the amount of amine

<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($cm^3/cm^2/s$)				
			cotton	Nylon	PET	Acryl	Silk
Un mordant	-	-	104	36.6	14.6	101	202
Mordant	$CuSO_4$	0(After mordant)	60.0	26.9	15.1	59.1	196.7
	$CuSO_4$	1	57.1	25.6	16.9	59.5	238.8
	$CuSO_4$	2	54.3	27.0	17.2	61.5	218.0
	$SnCl_4$	0(After mordant)	60.8	27.6	16.1	61.7	202.8
	$SnCl_4$	1	56.8	27.4	16.6	59.5	199.0
	$SnCl_4$	2	62.6	28.6	16.6	64.4	234.3
	$Alk(SO_4)_2$	0(After mordant)	75.8	26.3	15.8	64.9	192.5
	$Alk(SO_4)_2$	1	74.2	28.3	15.5	79.7	198.0
	$Alk(SO_4)_4$	2	72.4	27.6	15.2	72.4	204.8
	$FeCl_3$	0(After mordant)	77.6	27.5	14.3	75.9	200.1
	$FeCl_3$	1	75.0	27.0	15.2	66.7	202.8
	$FeCl_3$	2	77.1	23.6	15.6	77.4	204.2
	$Cr(NO_3)_3$	0(After mordant)	76.1	26.5	16.2	67.5	200.7
	$Cr(NO_3)_3$	1	74.4	26.7	15.0	77.1	208.7
	$Cr(NO_3)_3$	2	74.7	27.0	14.9	70.5	208.0

end groups in the molecules is rather low. Due to the low capability of the nylon molecules toward the metal ions, different from the cottons fabrics, nylon fabrics do not show absorption capability differences between the group of (Cu, Sn), and the group of (Al, Fe, Cr).

Next, in the case of PET fabrics, the inferences deduced from the results of the nylon specimens, a synthetic fiber, seems to be more accurate. The air-permeability decrease is not observed at all according to the metal ion absorption of the PET fabrics. Compared to the nylon fibers, the PET fibers have much higher crystallinity, and the functional groups capable of forming linkage with the metal ions in the PET are negligible. Therefore, it is concluded that none of the five metal ions are absorbed in the PET fabric specimens.

In the case of acrylic fabrics, another synthetic, unexpected results come forth compared to the nylon and PET fabric specimens. Acrylic fibers are extremely crystalline and have few functional end groups to make links with metal ions. Nonetheless the air-permeability of the mordanted acrylic fabric specimens showed almost the same amount of decrease with those of the cotton fabrics. The special tendency is, however, plausible when we consider the chemical structures of the acrylic fibers.

100% acrylic fibers can not be dyed well, of course. The fact that commercial acrylic fibers for apparels are copolymers of acrylonitrile and acrylic acid may explain the above mentioned phenomenon.

We may explain that the selective absorption behaviors between the (Cu, Sn) group and (Al, Fe, Cr) group and cotton fibers are expedited by the -COOH group. At the same time, there is a positive correlation between the amount of metal ion absorption and the decrease of air-permeability.

It has been known that silk fibers have good metal ion absorption capability regardless of the types of metal ions since the silk fibers are made of proteins. The reason that there is no change in the air-permeability after the mordanting might be that the silk fabric specimen is too thin.

Due to the fact that the weave structure of the silk specimen is open, even though enough amount of metal ion absorption might have taken place in the silk fibers, the absorption may not have affected the change of air-permeability.

This inference for the silk fabric behavior may well be supported by the result of the test after dyeing that will be described later on in this study.

We will investigate the change of air-permeability according to rinsing after the mordanting. It is expected that the air-permeability will increase a little or change anyway if the absorbed metal ions are detached from the fabric by the subsequent rinsing procedure considering the fact that the absorption of the metal ions on the fiber decreased the air-permeability.

In the case of cotton fabrics, the rinsing procedure decreased the air-permeability by a small margin (the case of Cu), or showed no effect on the air-permeability. In the case of Cu, the reason of the decrease of the air-permeability might be that the rinsing procedure may possibly have made the fabric structure denser.

As a whole, it may be judged that, in the case of cotton fabric specimens, the rinsing procedure did not have detached the metal ions including Cu since there was not much of change in the air-permeability after the mordanting with subsequent rinsing.

The fact that the rinsing procedure did not accompany the detachment of metal ions meant that there was not excessive amount of metal ions on the fabric specimens. In the case of cotton fibers, the concentration values of Cu, Sn, Al corresponding to 2%, 2%, 5% may not have induced excessive absorption of metal ions.

In the cases of nylon and PET, the air-permeability values did not decrease after the mordanting and subsequent rinsing procedure. This may indicate that the amount of metal ion absorption was not so excessive to the extent that might have induced the detachment of the metal ions by rinsing. It is expected that since the capability of absorption in the cases of nylon and PET fabrics is especially low, the probability that the metal ions absorbed on the corresponding fiber surface may be detached from the fiber may also be low.

In the case of acrylic fabric specimens, there was a tendency of the air-permeability increase after the mordanting and subsequent rinsing. Compared to the nylon and PET fabrics, it was evidenced that there was a large amount of metal ion absorption in the acrylic fabric specimens. Especially for Al and Cr, the air-permeability clearly increased after the rinsing procedure. It is, therefore, highly probable that the excessive metal ions absorbed to the -COOH groups may be detached.

In the case of silk fabrics, though there were several cases of the air-permeability increases, these do not seem convincing. This phenomenon may have been induced by the fact that the thickness of the silk fabric specimen is too low. As a whole, in the case of silk fabrics, the change of the air-permeability of the fabrics by the rinsing is negligible.

Considering all the above, metal ions don’t seem to be excessively absorbed on the surface

<Table 2> Air-permeability of cochineal dyed fabrics, cotton and silk

Application of Mordanting	Mordant	number of rinsings after mordanting	Fabric	
			Cotton	Silk
Un mordant	control(grey)	-	104	202
	dyed fabric	-	60	200
Mordant	$CuSO_4$	0(After mordant)	76.3	184.3
	$CuSO_4$	1	74.3	183.7
	$CuSO_4$	2	74.5	187.3
	$SnCl_2$	0(After mordant)	71.7	184.7
	$SnCl_2$	1	73.8	186.2
	$SnCl_2$	2	72.2	189.8
	$Alk(SO_4)_2$	0(After mordant)	69.9	179.8
	$Alk(SO_4)_2$	1	62.6	188.8
	$Alk(SO_4)_2$	2	74.0	189.0

of fibers at the concentrations of 2%, 2%, 2%,2%, 5% for the Cu, Sn, Fe, Cr, Al, respectively. The degree of detachment of the metal ions is not appreciably high in the rinsing procedure after the mordanting of the fabrics.

Next, <Table 2> shows the air-permeability of the cotton and silk fabric specimens after dyeing with cochineal dyestuff.

In the case of unmordanted fabrics, the air-permeability values of cotton and silk fabrics after dyeing were 60 and 200, respectively. In the case of cotton fabrics, there was a significant decrease of air-permeability as a consequence of the dye absorption in the fiber. In contrast, the air-permeability did not decrease at all after the dyeing procedure only in the case of silk fabrics.

In the case of cotton fabrics, as shown in <Table 2>, mordanting procedure gave rise to the increase of air-permeability of about 10~15 regardless of the types of mordanting agents, compared to the unmordanted fabrics. The reason for the increase of the air-permeability is that the metal ions and the dyestuffs form coordinate bond complexes. It is elucidated that compared to the case of simple absorption by physical route in the cotton fibers, the case of forming three-dimensional coordinate bond complexes among the cotton molecules, dyestuffs, and metal ions have resulted in the increase of the air-permeability.

In the case of cotton fibers, as already shown in the <Table 2>, the air-permeability values were maintained around at 60, when the fabrics were mordanted with Cu and Sn. However, the air-permeability increased more than 15 after the dyeing procedure. This clarifies that the insoluble coordinate bond complexes are acting upon the increase of the air-permeability.

In the case of silk fabrics, the tendency is different from the case of cotton fabrics.

In the case of silk fabrics, the air-permeability did not decrease at all, if the fabric is mordanted only, or dyed with cochineal under the unmordanted state. However, the air-permeability dropped significantly after the dyeing of the mordanted fabrics.

It is expected that the bonds between the fiber molecules and the metal ions are stronger since the silk proteins are able to form strong bonds with the metal ions different from cotton fiber molecules. Moreover, the silk fibers develop dark shade during the dyeing with cochineal without the aid of mordanting procedure. It is expected, therefore, that the coordinate bonds among silk molecular chains, metal ions, and dyestuffs in the mordant-dyeing are different from those among cotton fibers.

As mentioned before, however, the thickness of the silk fabrics is so low that the credibility of the change of the air-permeability is not high enough. This leads to a further experimental study in order to confirm the trend.

It is hard to notice the change of the air-

<Table 3> Color measurement of cotton fabric specimens

Application of Mordanting	Mordant	number of rinsings after mordanting	Color Difference			
			L*	a*	b*	ΔE
Un mordant	control(grey)	-	92.1	-0.1	1.7	
Mordant	dyed fabric	-	88.1	5.6	5.4	7.91
	$CuSO_4$	0(After mordant)	78.6	12.3	-3.1	18.93
	$CuSO_4$	1	78.7	12.2	-3.3	18.82
	$CuSO_4$	2	79.0	11.8	-2.9	18.35
	$SnCl_2$	0(After mordant)	74.5	26.1	8.5	32.25
	$SnCl_2$	1	75.3	25.1	8.4	31.05
	$SnCl_2$	2	75.0	25.8	7.4	31.50
	$Alk(SO_4)_2$	0(After mordant)	78.4	17.2	-0.1	22.11
	$Alk(SO_4)_2$	1	77.5	18.1	-1.2	23.52
	$Alk(SO_4)_2$	2	77.9	17.7	-0.6	22.90

permeability values according to the number of rinsing procedures, if we look at the number of rinsings after mordanting. This confirms the fact that the metal ions did not detach from the fibers by rinsing, and that they did not absorbed on the surface excessively.

Next, the effect of mordanting is reviewed by comparing the color differences after the dyeing of cotton and silk fabric specimens. <Table 3> shows the color differences after the dyeing of cotton fabric specimens.

In the case of unmordanted dyeing, the ΔE value is 7.91, indicating there was no dye uptake. However, in <Table 2>, the decrease of the air-permeability was almost 40 after the unmordanted dyeing.

By referring to the values of ΔE and the air-permeability decrease, even if there was no dye uptake, the air-permeability did decrease. It is clear that not only the color component developing specific color decrease the air-permeability but also general color component absorption decrease the air-permeability. However, in case there was mordanting, the color development is expedited by the mordanting based on the fact that ΔE values of the fabrics increased, when using Cu, Sn, Al, with the increase of 18, 32, 23, respectively. This indicates that the color is developed by the formation of coordinate bond complexes between the metal ions and the specific color components. As shown in <Table 2>, mordanted fabric specimens show higher air-permeability values compared to the unmordanted fabric specimens. This in turn verifies that the three-dimensional coordinate bond complex formation increase the air-permeability.

The most important outcome of the <Table 3> is that the ΔE values are maintained constant regardless of the number of rinsings after mordanting for all the mordanting agents. If there were any detachment of the part of absorbed metal ions by the rinsing procedure, then the function of the mordanting might have become different, resulting in a ΔE value change.

The constant values of ΔE regardless of the number of rinsings may verify the following facts:

1) There was not excessive absorption of the

metal ions to cause the detachment of the metal ions by rinsing after the mordanting, since the concentration range of the Cu, Sn, Al mordanting agents was adequate.

2) The bonds between the cotton fibers and the metal ions are so strong that the metal ions are not detached by the subsequent rinsing procedure. This is an evidence that the adequate use of the mordants prevent the severe detachment by the rinsing.

<Table 4> shows the color difference values of the silk fabrics after dyeing.

Different from the cotton fabric case, the ΔE value of the fabric specimen reaches about 48 for unmordanted dyeing, which indicates the strong dye uptake of the cochineal dyestuff by the silk fibers. As shown in the <Table 2>, however, the air-permeability value does not decrease at all. This seems to be due to the fact that strong bonds are established between the silk fibers and the cochineal dyestuffs. Strong mordanting effects are distinct, since the ΔE values are increased to 66, 77, and 71 for the Cu, Sn, and Al mordanting, respectively. As shown in the cotton fabric cases, the rinsing effect after the mordanting did not develop.

IV. Conclusions

According to the experimental results by several researchers, it has been reported that the air-permeability values of most of the fabrics decreased by the mordanting procedure. Exact quantitative information, however, has not been presented so far. In this study, the change of the fabric air-permeability was investigated quantitatively. At the same time, the change of the fabric air-permeability according to the dyeing procedure.

In order to investigate the possibility of the detachment of the metal ions on the fiber or fabric surface, the change of the air-permeability was investigated after several rinsing of the mordanted fabrics. By comparing the color differences of the cochineal dyed fabrics, with differing number of rinsing procedure after mordanting, we arrived at the following conclusions.

1. After the mordanting procedure, the air-permeability values of the fabric specimens show a decreasing trend, even if there were minor differences according to the fiber materials and the types of mordants.

2. In the case of cotton fibers, the degree of air-permeability decrease is determined by the amount of metal ion absorption.

3. The air-permeability changes according to the metal ion absorption even if the fibers are made of the synthetic fibers(nylon, PET, acrylic). There is a positive correlation between the amount of metal ion absorption and the air-permeability decrease.

4. At the range of mordant concentration, 2% Cu, 2% Sn, 2% Fe, 2% Cr, 5% Al, the metal ions are not excessively absorbed on the fiber surface. Also, any remarkable detachment of the metal ions does not accompany after the mordanting with the subsequent rinsing procedure.

5. The air-permeability value decreases if the cochineal dyestuffs are taken up by the fibers under unmordanted state. This indicates that by the simple dye uptake the air-permeability may be reduced as in the case of mordanting procedure.

6. The air-permeability value decreases by a simple mordanting procedure or unmordanted

dyeing procedure. If, however, mordant-dyeing is finished, it significantly increases the air-permeability compared to the former two cases. We presume that some three-dimensional coordinate bond complexes are established among the fiber molecular chains, dyestuffs, and metal ions.

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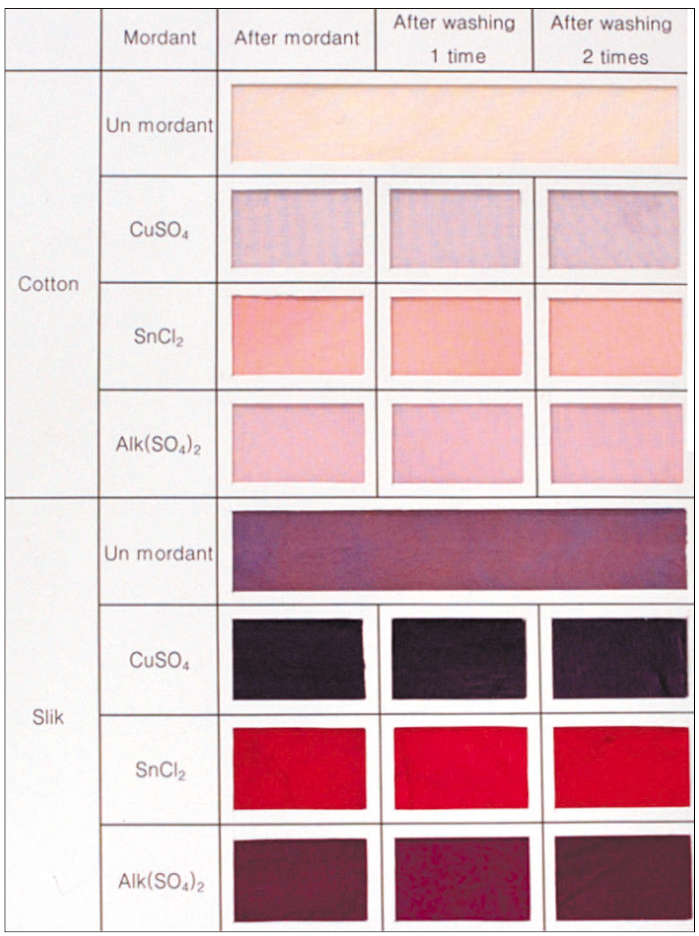
Received 2 November, Accepted 29 November.



Appendix. Fabric specimens dyed with cochineal dyestuff