

CHARACTERISTICS OF ALDEHYDE REACTIVE DYES FOR LEATHER DYEING AND RETANNING PROCESS

by

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ABSTRACT

Dyeing and re-tanning properties of nine aldehyde reactive dyes synthesized in our previous work were studied using aluminum pretanned wet-white sheep leather as a substrate. Their washing fastness and four dyeing property indexes, i.e., substantivity (S), exhaustion (E), reactivity (R) and fixation (F) were measured. The relationship between the color-matching effect and the relative difference values of the four dyeing property indexes of the combined dyes were investigated, and the simultaneous tanning-dyeing property of reactive dyes with a glutaraldehyde backbone were tested. The results were as follows: (1) The synthesized aldehyde reactive dyes could dye wet-white leather under mild conditions ($T = 35\text{--}45^\circ\text{C}$, $\text{pH} = 4.0\text{--}6.5$) within 1.5 h, and the dyed leather possessed a satisfactory washing-fastness. (2) Reactive dyes with a glutaraldehyde backbone had better dyeing performance than mono-aldehyde reactive dyes. (3) The less the relative difference value of the dyeing property indexes of the combined dyes, the better was the color-matching effect. (4) The tested reactive dyes with a glutaraldehyde backbone increased the T_s of wet-white leather to $11\text{--}17^\circ\text{C}$ in addition to dyeing it to the corresponding color.

INTRODUCTION

The idea of aldehyde reactive dyes derived from the research of our laboratory on the color-forming mechanism of natural iridoids (such as genipin, loganin aglycone, oleuropein aglycone and E-6-O-methoxycinnamoyl scandoside methyl ester aglycone) with primary amino ($-\text{NH}_2$) containing materials (such as leather, silk and wool).^{1,2} This mechanism involved an inter-conversion isomer with a glutaraldehyde backbone in the reaction system, which caused genipin, for example, to crosslink with collagen fiber through a Schiff's reaction (Figure 1). Two effects occurred during this process: collagen fiber was dyed to dark-blue and its hydrothermal stability was increased.³

Glutaraldehyde is a commonly used tanning agent for leather manufacture. It was generally thought that a crosslinking reaction occurred between glutaraldehyde and collagen molecules through a Schiff's reaction during the tanning process,⁴ similar to that of genipin with collagen fiber. This suggested to us that a new kind of reactive dye could be developed by "grafting" bio-friendly colorants to the backbone of glutaraldehyde (Figure 2). Theoretically, a simultaneous tanning-dyeing process could be achieved by applying this novel kind of reactive dye to leather.

EXPERIMENTAL

Brief Introduction for the Preparation of Aldehyde Reactive Dyes

Generally, glutaraldehyde is preserved as a 25% or 50% aqueous solution and it is almost impossible to "graft" colorant compounds to its backbone directly. So an "easy to difficult" strategy was adopted, during which colorant compounds were "grafted" to the $\alpha\text{-C}$ of n-butyl-aldehyde or the methyl-C of 3-(4-methyl) phenyl -acrylaldehyde, so that a series of reactive dyes with mono-aldehyde as the reactive group was obtained (Figure 3), their capacity of dyeing collagen fiber were investigated to confirm the feasibility of this novel sort of reactive dye.

After that, two synthesis routes were chosen to "graft" colorant compounds to the precursors of glutaraldehyde, and target products were obtained by an oxidation or hydrolysis reaction (Figure 4). Nine aldehyde reactive dyes were prepared and their molecular structures, molecular weight, color and the wavelength of maximum absorption (λ_{max}) are listed in Table I; detailed information about the synthesis process and identification methods is available in our previous publications.⁵⁻⁹

The Measurement of S, E, F and R (Taking D₇ as an Example)¹⁰

Aluminum pre-tanned wet-white sheep leather (5 cm $\times$ 5 cm, provided by the Leather Department of Sichuan University,

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China) was weighed and the weight was used as a reference for other reagents: water 300% (w/w), D_7 2% (w/w). The pH of the dye-bath was adjusted to 6.0-6.5 with 10% (w/v) Na_2CO_3 aq. and the leather pelt was dyed for 30 min at 35-40°C. The pH was then adjusted to 4.0-4.5 with 10% (v/v) HAc aq. and the pelt was dyed for another 60 min at 45°C. The nine sampling points for measuring the exhaustion and fixation values are shown in Figure 5.

The values of S, E, F and R could be obtained by three steps, as below:

Calculation of exhaustion (E_t): In each sampling points 1-9, the absorbance (A_t) of the diluted dye solution was measured at λ_{max} (634 nm for D_7) using a TU-1901 UV-Vis spectrophotometer; the exhaustion value of the dye at a sampling points (E_t) was calculated as below:

$$E_t = (1 - A_t/A_0) \times 100\%$$

where A_t and A_0 are the absorbance values of the dyeing-bath at the sampling point and time zero, respectively.

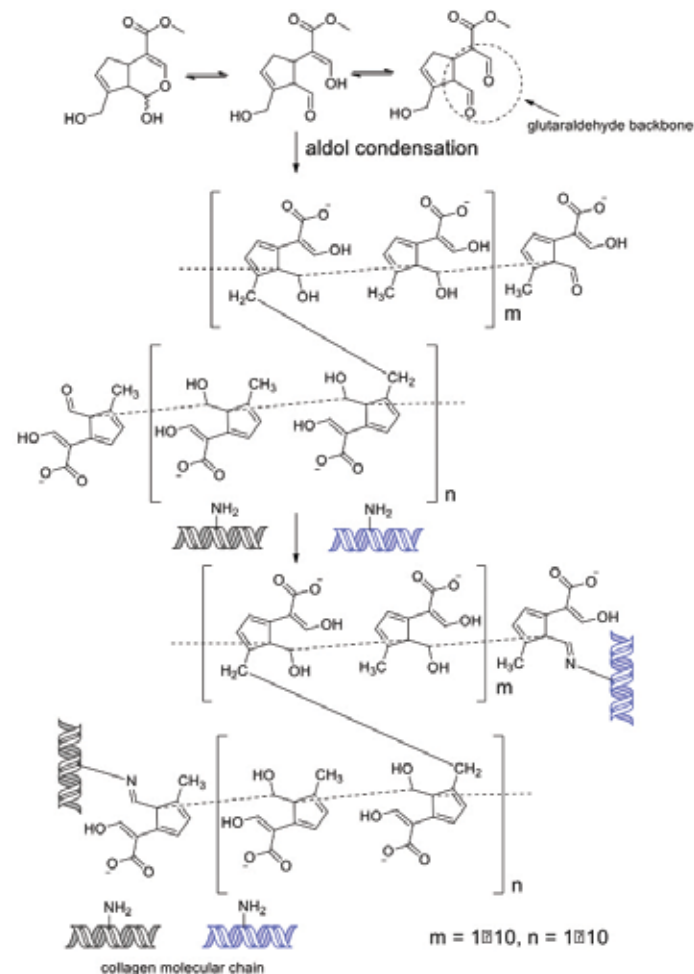


Figure 1. The crosslinking and color forming mechanism of genipin with collagen.

Calculation of fixation (F_t): At sampling points 1-9, the dyed leather sample was removed and soaped-off using a weakly anionic detergent (2 g/L) at 40°C for 10 min. The rinsate was diluted to bring the absorbance into the range of the spectrophotometer and its absorbance value (A_t) was measured at λ_{max} . The fixation value of the dye at that sampling point (F_t) was calculated as below:

$$F_t = (1 - A_t/A_0) \times 100\%$$

where A_t and A_0 are the absorbance values of the soap-bath for a sampling points and the original dye-bath (2 g/L detergent was added also), respectively.

Drawing up the exhaustion and fixation curve: Making dyeing time as the X-axis and E_t and F_t as the Y-axis, the exhaustion and fixation curves of D_7 was achieved (Figure 6). According to Figure 6, S (substantivity), E (exhaustion), R

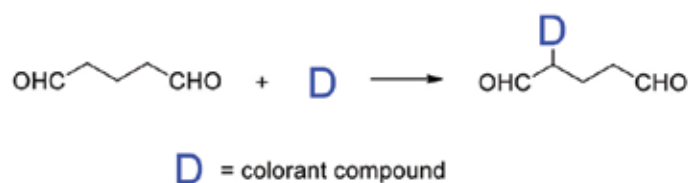


Figure 2. Grafting of colorant compound to glutaraldehyde backbone.

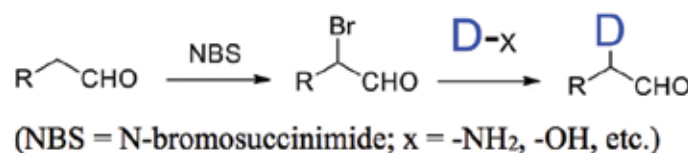


Figure 3. The synthesis route for mono-aldehyde reactive dyes



Figure 4. Two synthesis routes for reactive dyes with glutaraldehyde backbone.

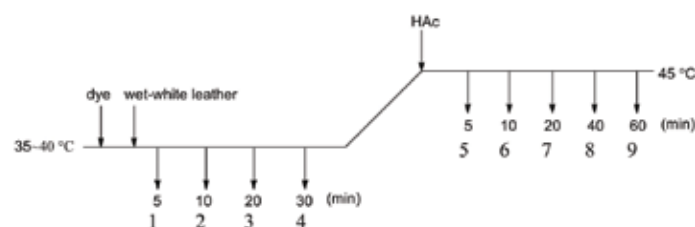


Figure 5. Nine sampling points for measurement of exhaustion and fixation.

(reactivity) and F (fixation) of D_7 could be obtained, where the value of S refers to the exhaustion value when $t = 30$ min; R refers to the value of fixation when $t = 35$ min, i.e. 5 min after addition of HAc; E and F refer to the final values of exhaustion and fixation, respectively. The values of S, E, F and R of the other eight dyes were obtained in the same way as above. These values are very useful in dyeing practice, especially for the choice of combined dyeing process when two or more than two dyes need to be mixed.

Measuring of Washing Fastness¹⁰

One piece of aluminum pre-tanned sheep wet-white (5 cm × 5 cm) was dyed by each dyestuff as described in Section 2.2, and the dyed pelt was then rinsed with distilled water and put in a 250-mL flask. After JFC, a non-ionic surfactant (1 g), and distilled water (50 mL) were added, the flask was shaken in a 25°C water bath. At each interval (0, 15, 30, 45, 60 min), a 1 mL soap-bath sample was drawn and diluted to bring the absorbance into the range of the spectrophotometer and its CIE $L^*a^*b^*$ color indexes, L_t , a_t and b_t were measured with a PFX195 Colorimeter. The chromatic aberration value (ΔE_t) at each interval was calculated as below:

$$\Delta E_t = ((\Delta L_t)^2 + (\Delta a_t)^2 + (\Delta b_t)^2)^{1/2}$$

where $\Delta L_t = L_t - L_0$; $\Delta a_t = a_t - a_0$; $\Delta b_t = b_t - b_0$; L_0 , a_0 , b_0 were the CIE $L^*a^*b^*$ color indexes of the original soap-bath.

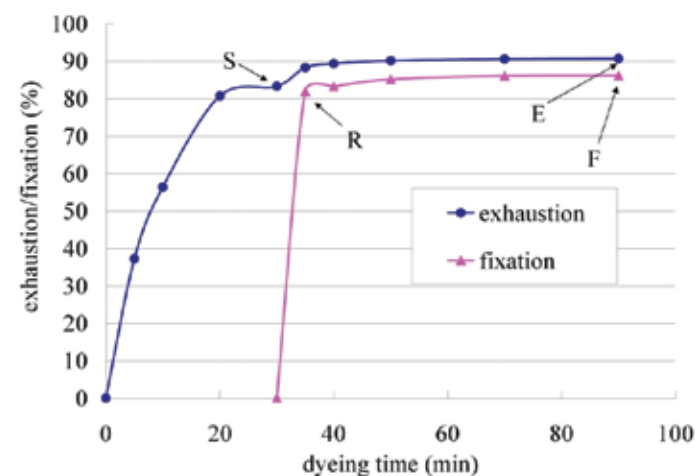


Figure 6. The exhaustion and fixation curve of D_7 .

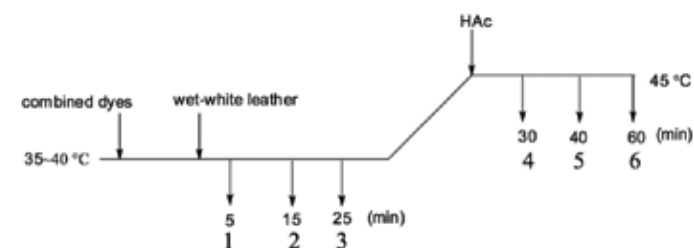


Figure 7. Six intervals of dyeing-bath sampling during combined dyeing experiment.

If $\Delta E_t < 0.5$ at 60 min, the washing fastness is grade 4; if $\Delta E_t < 0.4$ at 60 min, the washing fastness is grade 5.¹⁰

Combined Dyeing Experiment with Two Aldehyde Reactive Dyes (D_1 with D_7 , and D_5 with D_7)¹⁰

The dosage of each dyestuff was 1% (w/w, the total dosage was 2%), and the dyeing process was the same as that in Section 2.2. The proportion of each dyestuff in the remaining dyeing bath was calculated by three steps as below:

Measuring the absorbance value of each dyestuff: At each interval of 1-7 in Figure 7, a 1 mL dyeing-bath sample was drawn and diluted to bring the absorbance into the range of the spectrophotometer and its absorbance, $A_{R \max}$ and $A_{B \max}$ at $\lambda_{R \max}$ and $\lambda_{B \max}$ were measured using a TU-1901 UV-Vis spectroscopy, where $\lambda_{R \max}$ and $\lambda_{B \max}$ were the $\lambda_{\max}$ for each dyestuff.

Determining the absorption coefficient (K) of each dyestuff: For each dyestuff, an aqueous solution of concentration 0.1-0.5% (w/v) was prepared; its absorbance (A) at $\lambda_{R \max}$ and $\lambda_{B \max}$ were measured using a TU-1901 UV-Vis spectrophotometer, then K_R^1 , K_B^1 and K_R^2 , K_B^2 was calculated according $K=A/bc$, where $b=1$ cm and c is the concentration (g/L).

Calculation of C_R , C_B : The following equations were used to determine the concentrations of individual dyestuff (C_R and C_B) in the remaining dyeing-bath mixture:

$$A_{R \max} = K_R^1 b C_R + K_R^2 b C_B \text{ (at } \lambda_{R \max} \text{)}$$

$$A_{B \max} = K_B^1 b C_R + K_B^2 b C_B \text{ (at } \lambda_{B \max} \text{)}$$

Calculation of P_R and P_B :

$$P_R = C_R / (C_R + C_B) \times 100\%$$

$$P_B = C_B / (C_R + C_B) \times 100\%$$

where P_R and P_B was the proportion of each dyestuff in the dyeing-bath, respectively.

Simultaneous Tanning-Dyeing

For dyestuffs D_5 - D_9 , which had a glutaraldehyde backbone, the simultaneous tanning-dyeing experiments were performed as follows: aluminum pre-tanned sheep wet-white pelt (5 cm × 5 cm) were weighed and put in a 100-mL flask and 300% water, 3% dyestuff (both based on the weight of wet-white pelt) were added. The flask was shaken for 2 h in a 35°C water-bath, the pH was then raised to 5.0 with 10% Na_2CO_3 (w/v) and the flask was shaken for 1 h; pH was then raised to 6.5 and the flask was shaken for another 2 h. The simultaneous tanning-dyeing process was completed and the leather pelt was rinsed. The shrinkage temperature (T_s) of the treated pelts and aluminum pre-tanned sheep wet-white (control sample) was measured using a MSW-YD₄ (Shan-xi University of Science and Technology, P. R. China).

RESULTS AND DISCUSSION

The Advantage for the Dyeing Process of the Dyes

We found that the nine reactive aldehyde dyes could dye wet-white leather at 35-45°C and pH=4.0-6.5 within 1.5 h. This condition is relatively mild compared with the conditions required by commonly used reactive dyes at present; furthermore, no neutral salts were needed during the dyeing process. So, energy was saved and the environmental pollution from wastewater was reduced. On the other hand, it is well known that, one of the most disadvantages of commonly used reactive dyes is the hydrolysis of their reactive groups in the process of storage and application;¹¹ however, aldehyde

reactive dyes overcome this problem, because its reactive group, -CHO, do not react with water and therefore do not hydrolysis neither in the process of storage nor during application.

The Washing Fastness and S, E, R, F Values

Correlation of ΔE_t with washing time for D₁, D₅ and D₉ were shown in Figure 8. For D₁, whose $\Delta E_t < 0.5$, its washing fastness reached grade 4; for D₅ and D₉, whose $\Delta E_t < 0.4$, its washing fastness reached grade 5. The washing fastness of the other six-aldehyde reactive dyes were obtained in the same way and listed in Table II.

TABLE I

Molecular structures, molecular weight (MW), color and $\lambda_{\max}$ of nine reactive aldehyde dyes.

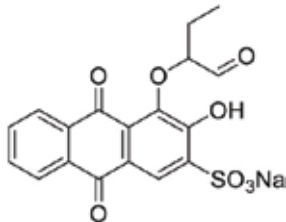
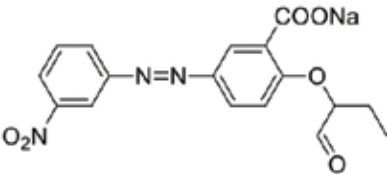
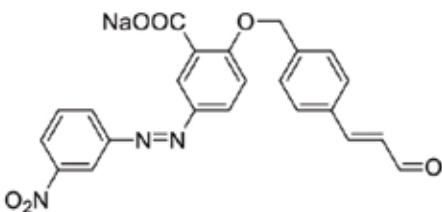
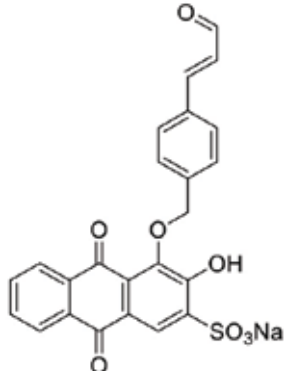
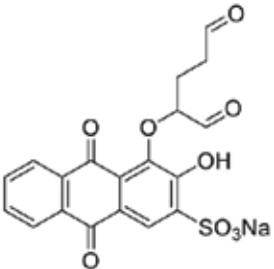
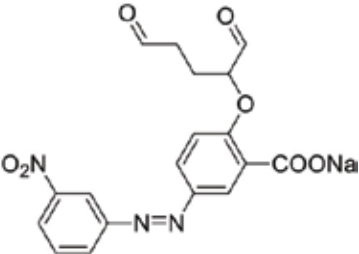
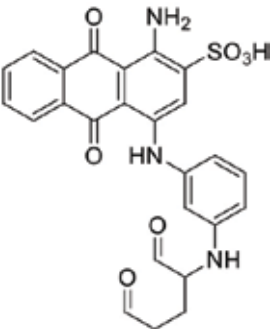
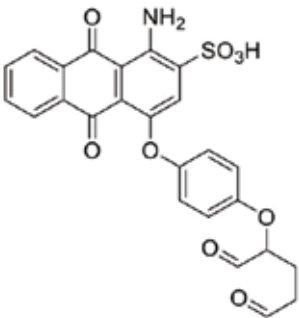
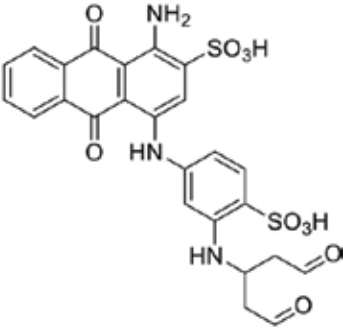
compound	structure	MW	color	$\lambda_{\max}$ (nm)
D ₁		412	purple-red	525
D ₂		379	yellow	353
D ₃		453	yellow	381
D ₄		486	red	535

Table I continues on following page.

Table I continued.

D ₅		440	red	522
D ₆		408	yellow	361
D ₇		507	blue	634
D ₈		509	purple-red	498
D ₉		587	black	even absorption within 400-600

From Table II, it is evident that, S, E, R and F values of the five reactive dyes with glutaraldehyde backbone were superior to those of mono-aldehyde reactive dyes. Nevertheless, washing fastness values for all of the nine reactive dyes reached grade 4 and possessed the fundamental property of reactive dyes.

The washing fastness values of the five reactive dyes with a glutaraldehyde backbone reached grade 5, i.e., the highest grade.

Results of Combined Dyeing Experiments

Two pairs of dyestuff, D₁ and D₇, D₅ and D₇ were chosen for the

TABLE II
Values of S, E, R, F (%) and washing fastness of nine reactive dyes
(mean of values from three experiments.)

dyes number	S	E	R	F	washing fastness (grade)
D ₁	52.54	57.87	48.35	52.17	4
D ₂	55.73	61.07	50.94	56.21	4
D ₃	60.35	65.27	53.74	59.86	4
D ₄	58.43	63.21	51.25	57.33	4
D ₅	84.22	91.37	82.05	83.27	5
D ₆	85.47	88.33	82.85	84.12	5
D ₇	83.26	90.65	81.93	86.14	5
D ₈	82.54	89.77	81.47	85.92	5
D ₉	85.25	92.13	82.76	84.32	5

TABLE III
The proportions of D₁ and D₇ in the dyeing bath at different intervals (%)
(mean of values from three experiments.)

Intervals	1 (5 min)	2 (15 min)	3 (25 min)	4 (30 min)	5 (40 min)	6 (60 min)
D ₁	48.15	51.29	59.32	63.76	66.80	72.28
D ₇	51.85	48.71	40.68	36.24	33.20	27.72

TABLE IV
The proportions of D₅ and D₇ in the dyeing bath at different intervals (%)
(mean of values from three experiments.)

Intervals	1 (5 min)	2 (15 min)	3 (25 min)	4 (30 min)	5 (40 min)	6 (60 min)
D ₅	52.2	52.2	52.2	50.0	50.2	51.8
D ₇	47.8	47.8	48.7	50.0	49.8	48.2

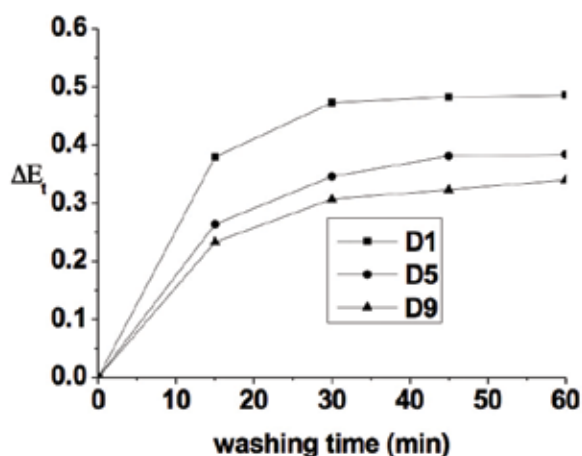


Figure 8. Correlation of ΔE_l with washing time for three aldehyde reactive dyes .

TABLE V
Relative difference value of dyeing property indexes between the two combined dyes.

	D_s (%)	D_E (%)	D_R (%)	D_F (%)
D_1 & D_7	45.24	44.14	51.55	49.12
D_5 & D_7	1.15	0.79	0.15	3.39

TABLE VI

The simultaneous tanning-dyeing property of reactive dyes with glutaraldehyde backbone (mean of values from three experiments.)

Dyes No.	wet-white	D_5	D_6	D_7	D_8	D_9
MW	-	440	407	507	531	587
Ts (°C)	73.2	86.5	84.3	87.8	87.4	90.6
color	white	red	yellow	blue	purple-red	black

combined dyeing experiments; their proportions in the dyeing bath at various intervals were shown in Table III and Table IV respectively.

It was evident from Table III that when D_7 (a blue reactive dye with a glutaraldehyde backbone) was combined with D_1 (a red mono-aldehyde reactive dye) to dye wet-white leather, the proportion of D_1 in the dyeing bath increased as the dyeing process proceeded and that of D_7 decreased. After 60 min, the proportions of D_1 and D_7 in dyeing bath were 72.28% and 27.72%, respectively. This result indicated that D_7 reacted with and was more readily adsorbed by wet-white leather than D_1 was; this induced the color of the dyed leather to stray from classical color-matching principles. In fact, the wet-white leather was dyed to a purple-blue color, although it should have been dyed to a purple color according to classical color-matching principles.

From Table IV, it is evident that when D_7 was combined with D_5 (a red reactive dye with a glutaraldehyde backbone) to dye wet-white leather, the proportions of D_5 and D_7 in the dyeing bath remained almost the same. This result indicated that the adsorption and reactive properties of D_5 and D_7 with wet-white leather were similar. This induced the color of the dyed leather

to follow classical color-matching principles, and the wet-white leather was dyed to purple, just as expected according to classical color-matching principles.

In order to give a quantitative analysis of the above results, the relative difference values of the four dyeing property indexes between the two combined dyes were calculated. For example, the relative difference value of substantivity (S) between D_1 and D_7 was calculated as below:

$$D_{S1\&7} = \frac{|S_1 - S_7|}{\frac{S_1 + S_7}{2}} \times 100\%$$

$$= |52.54 - 83.26| / (52.54 + 83.26)/2 \times 100\% = 45.24\%$$

The relative difference values of substantivity (S) between D_5 and D_7 was calculated in the same way:

$$D_{S5\&7} = \frac{|S_5 - S_7|}{\frac{S_5 + S_7}{2}} \times 100\%$$

$$= |84.22 - 83.26| / (84.22 + 83.26)/2 \times 100\% = 1.15\%$$

The relative difference value of the other three dyeing property indexes between two combined dyes, D_E , D_R and D_F are summarized in Table V.

It was clear that the relative difference values of the four dyeing property indexes between D_5 and D_7 were much smaller than those of D_1 and D_7 . We deduced that a good color-matching effect would be achieved only when the relative difference values of the four dyeing property indexes between the combined dyes were small.

Tanning Property of Reactive Dyes with Glutaraldehyde Backbone

Table VI showed that the five reactive dyes with a glutaraldehyde backbone had an obvious tanning effect for wet-white leather. When the dosage of each dye was 3% of the weight of wet-white, the increase of T_s for the treated leather varied from 11-17°C, and it had a positive correlation with the molecular weight of the dyes.

CONCLUSIONS

(1) The dyeing of wet-white leather with aldehyde reactive dyes indicated that the dyeing process could be undertaken at relatively mild conditions of 35-45°C, pH=4.0-6.5 within 1.5 h; all of the washing fastness values of the nine reactive dyes reached grade 4 and possessed the fundamental property of reactive dyes.

(2) S, E, R and F values of the five reactive dyes with a glutaraldehyde backbone were superior to those of mono-aldehyde reactive dyes, and their washing fastness values reached the highest grade, i.e., grade 5.

(3) During the combined dyeing process when two dyes were used, a good color-matching effect could not be achieved if the relative difference values of S, E, R and F values from the combined dyes were too large; the less the relative difference values of the dyeing property indexes of the combined dyes, the better was the color-matching effect.

(4) The tested reactive dyes with a glutaraldehyde backbone could be regarded as poly-functional leather chemicals, they could increase the T_s of wet-white leather to 11-17°C as well as dye leather to their corresponding color.

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