

Five Tanning-dyeing Processes Based on Triphenodioxazine (TPDO)

by

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Abstract

Triphenodioxazine (TPDO) is a high-performance chromophore. Based on TPDO, five simultaneous or combined tanning-dyeing processes were undertaken with pickled sheep pelt. Process 1 utilized a simultaneous tanning-dyeing material named TPDO-GT, a reactive dyestuff with aldehyde reactive groups which was prepared by grafting TPDO to the backbone of a glutaraldehyde-like compound (GT). The other four processes were combinations of TPDO with gallic acid (GA) and Al (III), Fe (III) salts, through treating the pelt using a different adding order. The adding order of Process 2 was to treat the pelt with Al (III) salt first and then the mixture of (TPDO+GA); that of Process 3 was to add the mixture of (TPDO+GA) first and then the Al (III) salt; that of Process 4 was to add Fe (III) salt first and then the mixture of (TPDO+GA); that of Process 5 was to add the mixture of (TPDO+GA) first and then Fe (III) salt. Tanning-dyeing effects of the five processes were compared, and the results were as follows: For hydrothermal stability (T_d from DSC analysis), $2 > 3 > 4 > 1 > 5$; for colors, 1 was purple-red, 2 was dark purple, 3 was red brown, 4 was dark green, 5 was brown back; for washing fastness, $1 > 2 > 3 \approx 4 > 5$.

Introduction

The first commercial reactive triphenodioxazine (TPDO) dye, C.I. Active Blue 163, was produced by ICI in the 1960s.¹ This kind of reactive dye has many useful features, such as high bright color, high color values, and excellent light fastness. Similar to most commonly used reactive dyes, the reactive group of normal TPDO reactive dyes includes dichloro-s-triazine and sulphatoethylsulphone.^{2,3} However, research results^{4,5} showed that two drawbacks exist in the currently available reactive dyes: (1) hydrolysis of their reactive group during the process of storage and application led to losses as high as 20-50% of reactive dyes; (2) a large quantity of neutral salts (20-40 g/l) were required during the dyeing process and this may cause serious environmental pollution. In order to solve these dilemmas, we previously developed a series of novel reactive dyes with glutaraldehyde as the reactive group.⁶ Unlike commonly used

reactive dyes, these novel reactive dyes do not hydrolyze and neutral salts are not needed during their application. Theoretical and practical studies have confirmed that a simultaneous tanning-dyeing process could be achieved when this novel kind of reactive dye is applied to leather because of the tanning ability of glutaraldehyde.⁷

Tanning and dyeing are two important processes in leather manufacture. Tanning is the key process to transform hide to leather; dyeing can satisfy the practical needs of various leather products and improve appearance. During separate tanning and dyeing processes, the tanning agents and dyes are added step by step. The development of a novel simultaneous tanning-dyeing process could make it possible to undertake tanning and dyeing processes in one step, which could not only make the process simpler, but also reduce the demand for water and energy, and reduce the environmental impact of leather manufacture.⁷

With the increasing demand for chrome-free tanning technologies, many methods have been developed.⁸⁻¹⁰ Tannages combined with vegetable tannin-aluminum, vegetable tannin-aldehyde, and aluminum-aldehyde have been shown to be effective. The physical-mechanical properties of leather tanned by these combinations are adequate for a variety of applications and their hydrothermal stability is in the range of 85 °C to 100 °C.^{11,12}

In this study, based on TPDO, five chrome-free simultaneous or combined tanning-dyeing processes were undertaken with pickled sheep pelt. Washing fastness and hydro-thermal stability of the treated samples were investigated and compared.

Experimental

Materials

3,4-Dihydro-2H-pyran-2-methanol (AR) was purchased from Huachem Industry Ltd (Japan). 2, 5- diaminobenzenesulfonic acid (AR) and tetra-chloro-p-benzoquinone (AR) were purchased from Long-sheng Dye Chemical Corp (Zhejiang, China). Concentrated sulfuric acid (98%), N-bromosuccinimide (NBS), N,N-dimethylformamide (DMF), aluminum sulfate,

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ferric sulfate, gallic acid (GA), levelling agent O-25 and other commonly used chemicals were purchased from Chengdu Kelong Chemical Corp. Pickled sheep pelt and fatliquoring agent CNS were kindly provided by the Leather Science and Engineering Department of Sichuan University (China).

Synthesis of Triphenodioxazine (TPDO) and TPDO- GT

The synthesis routes for TPDO and TPDO- GT were described in Figure 1. The detail operation could refer to our previous work.¹³

Five Tanning and Dyeing Processes

Process 1: Simultaneous Tanning-Dyeing via TPDO-GT⁷

Pickled sheep pelt was weighed and the weight was used as a reference for the other reagents: 2.0% (w/w) TPDO-GT, 300.0% (w/w) water, 1.0% (w/w) leveling agent O-25 and 5.0% (w/w) fatliquoring agent CNS. The pH of the bath was adjusted to 6.5-7.0 with 10% (w/w) Na₂CO₃ (aq.), and the pelt was treated for 120 min at 40 °C. The pH was then adjusted to 4.0-4.5 with 10% (w/w) HAc (aq.), and treated for another 120 min at 50 °C. The treated pelt was washed twice with water and dried at room temperature (Figure 2).

Process 2: Combination of Al (III) + (TPDO+GA)¹²

The pelt was weighed and the weight was used as a reference for the other reagents: 300.0% (w/w) solution of Al₂(SO₄)₃ (5.1% Al₂O₃ to the weight of pelt). The pelt was tanned for 120 min at 30 °C. The pH of the bath was adjusted to 5.0 with 10% (w/w) Na₂CO₃ (aq.) and tanning was continued for another 60 min. Then, 1.0% (w/w) O-25, 5.0% (w/w) CNS, 2.3% (w/w) GA and 1.7% (w/w) TPDO were added. The pH of the bath was adjusted to 6.0, and the pelt was treated for 120 min at 35 °C. The pH was then adjusted to 3.0 with 10% (w/w) HAc (aq.), and the pelt was treated for another 120 min at 45°C. The treated pelt was washed twice with water and dried at room temperature (Figure 3).

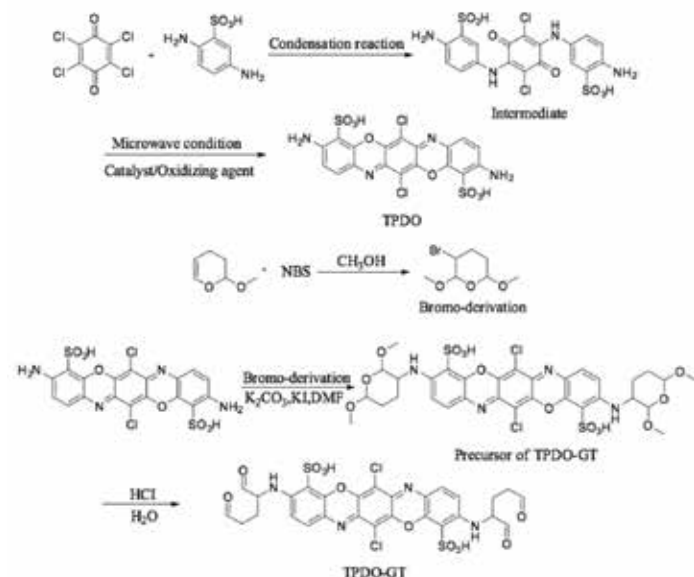


Figure 1. Synthesis of TPDO and TPDO-GT.

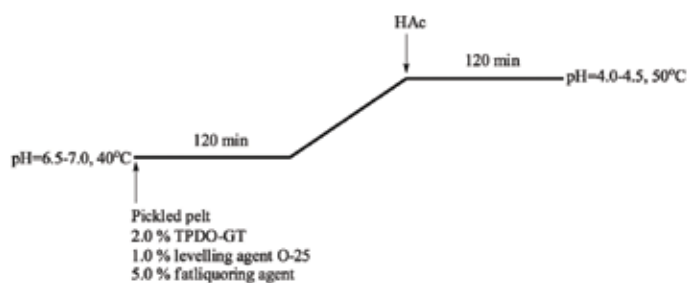


Figure 2. Process 1: Simultaneous Tanning-Dyeing via TPDO-GT.

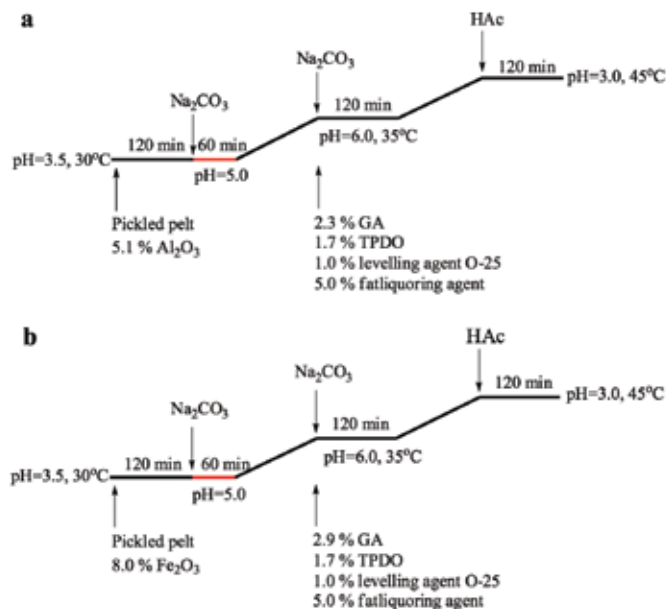


Figure 3. Process 2 and 4: Combinations of Al (III) + (TPDO+GA) (a) and Fe (III) (b) + (TPDO+GA).

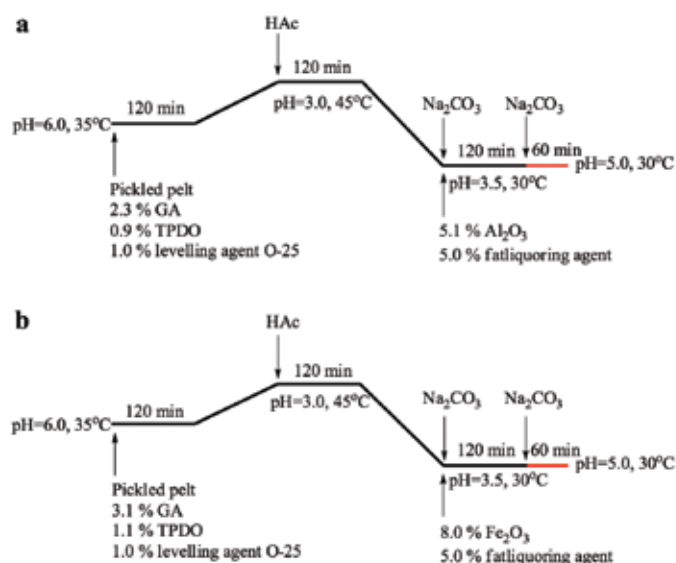


Figure 4. Process 3 and 5: Combination of (TPDO+GA) + Al (III) (a) and (TPDO+GA) + Fe (III) (b).

Process 3: Combination of (TPDO+GA) + Al (III)^{10, 12}

The pelt was weighed and the weight was used as reference for other reagents: 300.0% (w/w) water, 2.3% (w/w) GA, 0.9% (w/w) TPDO and 1.0% (w/w) O-25 were added. The pH of the bath was adjusted to 6.0, and the pelt was treated for 120 min at 35 °C. The pH was then adjusted to 3.0 with 10% (w/w) HAc (aq.) and the pelt was treated for another 120 min at 45 °C. Then, 5.1% (w/w) Al₂O₃, 5.0% (w/w) CNS were added, and the pelt was treated for 120 min at 30 °C. Finally, the pH was adjusted to 5.0 with 10% (w/w) Na₂CO₃ (aq.) and the pelt was tanned for 60 min. The treated pelt was washed and dried at room temperature (Figure 4).

Process 4: Combination of Fe (III) + (TPDO+GA)

The treatment process was the same as that of Process 2. The technique parameters are described in detail in Figure 3.

Process 5: Combination of (TPDO+GA) + Fe (III)

The treatment process was the same as that of Process 3. The technique parameters are described in detail in Figure 4.

Identification

Ultraviolet-visible (UV-vis) absorption spectra for determination of the λ_{\max} of TPDO and TPDO-GT were obtained using a TU-1901 (PERSEE, China).

Fourier transform infra-red (FTIR) spectra of TPDO and TPDO-GT were recorded between 4000 and 400 cm⁻¹ using KBr pellets on a FTS3000 FTIR spectrometer (DIGILAB, USA).

Electrospray ionization-high resolution mass spectra (ESI-HRMS) of TPDO and TPDO-GT were recorded with MeOH as solvent using an LTQ Orbitrap XL (Thermo Fisher Scientific, USA).

Differential scanning calorimetry (DSC) analysis of treated pelts was carried out on a USA TA Q2000 instrument. All samples were dried at room temperature and humidity. Approximately 5 mg of sample was heated in an aluminum pan from 25°C to 150°C at a rate of 5°C min⁻¹ under nitrogen atmosphere (flow 50 mL min⁻¹). Each measurement was repeated three times. The temperature at the peak of the DSC curve was regarded as the decomposition temperature (T_d) of the sample.

The washing fastness of the treated pelts was tested according to ISO 105-E01:2013, MOD.⁷

Results and Discussion

Identification of TPDO AND TPDO-GT

The analysis results from high resolution MS (HRMS) for TPDO and TPDO-GT were in good agreement with the calculated values. For TPDO: measured m/z 544.93781; calculated for C₁₈H₁₁Cl₂N₄O₈S₂⁺ (M+H)⁺, 544.93899. For TPDO-GT: measured

m/z 741.01398; calculated for C₂₈H₂₃Cl₂N₄O₁₂S₂⁺ (M+H)⁺, 741.01255. ESI-HRMS confirmed the feasibilities of the synthesis routes.

The FTIR spectrum of TPDO-GT (Figure 5 (b)) revealed a strong absorption at 1717 cm⁻¹ for the C=O of glutaraldehyde, as well as an absorption at 3378 cm⁻¹ due to the -NH- secondary amino group. In the spectrum of TPDO (Figure 5 (a)), the absorption due to the -NH₂ primary amino group occurred at 3430 cm⁻¹ and 3350 cm⁻¹.

In the UV spectrum of TPDO (Figure 6 (a)), λ_{\max} appeared at 593 nm, indicating a violet color, while λ_{\max} of TPDO-GT (Figure 6(b)) appeared at 534 nm, indicating a purple-red color. The “blue-shifting” of the color was due to the destruction of the conjugate structure of TPDO-GT which was transferred from TPDO (Figure 1).

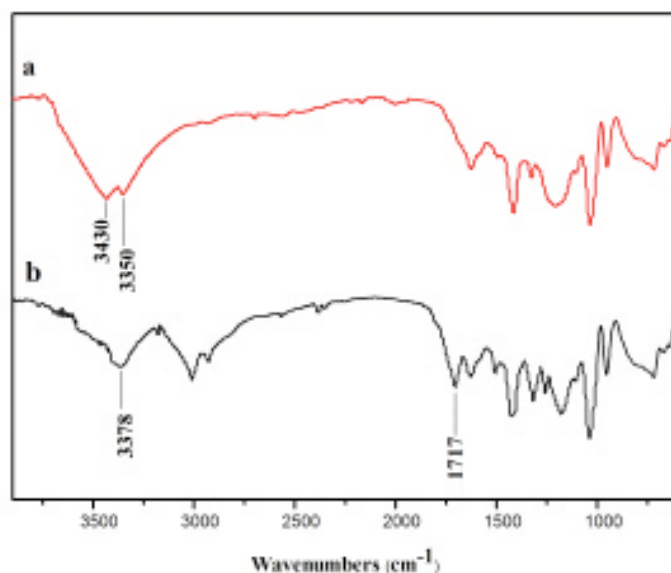


Figure 5. FTIR spectra of TPDO (a) and TPDO-GT (b).

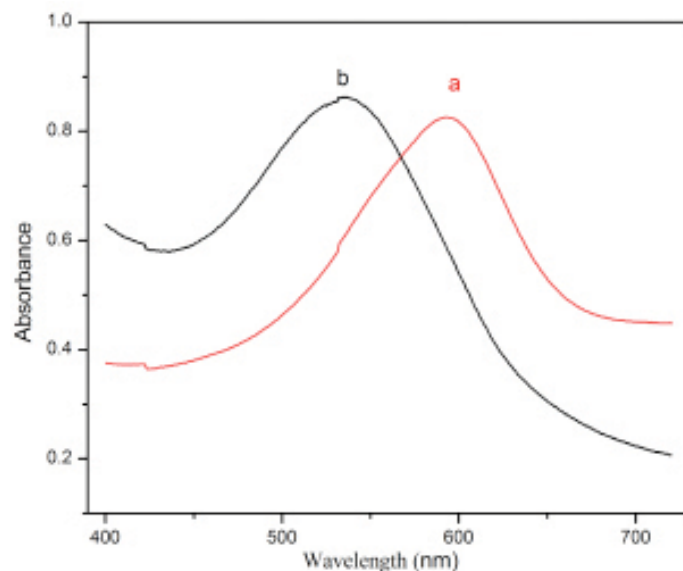


Figure 6. UV-vis absorbance of TPDO (a) and TPDO-GT (b).

Optimization of Process 2

To seek the optimum combination parameters of Process 2, i.e. the combination of Al (III) + (TPDO+GA), a three-factor (dosage of Al₂O₃, GA and TPDO) and three-level orthogonal experiment was designed. The parameters and results are shown in Table I. According to the values of R, we could deduce that, the dosage of GA (factor B) exerted the most significant effect on T_d of the treated pelt, and the order of importance of factors that influenced T_d was B > C > A. According to the values of K, we could deduce that, the optimal combination was A₂B₁C₃. i. e., the

Table I

L₉(3³) experiment parameters and results for Process 2.

Level	Factor (mass percentage based on pickled sheep pelt)		
	A (Al ₂ O ₃)	B (GA)	C (TPDO)
1	3.1% (A ₁)	2.3% (B ₁)	0.9% (C ₁)
2	5.1% (A ₂)	2.9% (B ₂)	1.1% (C ₂)
3	7.1% (A ₃)	3.1% (B ₃)	1.7% (C ₃)

Test Number	A (Al ₂ O ₃)	B (GA)	C (TPDO)	Td (°C)
1	1 (A ₁)	1 (B ₁)	3 (C ₃)	120.2
2	1	2 (B ₂)	2 (C ₂)	116.3
3	1	3 (B ₃)	1 (C ₁)	107.5
4	2 (A ₂)	1	1	115.6
5	2	2	3	119.0
6	2	3	2	113.0
7	3 (A ₃)	2	1	110.0
8	3	1	3	117.2
9	3	3	2	109.0
K1	344.0	353.0	333.1	
K2	347.6	341.3	338.3	
K3	332.2	329.5	356.4	
R	15.4	23.5	23.3	
Optimal level	A ₂	B ₁	C ₃	

dosages of Al₂O₃, GA and TPDO were 5.1%, 2.3% and 1.7% respectively. Parallel tests under this condition were made three times, and the average value of T_d was 121.2 ± 0.3°C.

Optimization of Processes 3,4 and 5

Similar work as above was undertaken to optimize Processes 3, 4 and 5. The parameters and results for each process are shown in Table II, Table III and Table IV.

Table II

L₉(3³) experiment parameters and results for Process 3.

Level	Factor (mass percentage based on pickled sheep pelt)		
	A (Al ₂ O ₃)	B (GA)	C (TPDO)
1	3.1% (A ₁)	2.3% (B ₁)	0.9% (C ₁)
2	5.1% (A ₂)	2.9% (B ₂)	1.1% (C ₂)
3	7.1% (A ₃)	3.1% (B ₃)	1.7% (C ₃)

Test Number	A (Al ₂ O ₃)	B (GA)	C (TPDO)	Td (°C)
1	1 (A ₁)	1 (B ₁)	1 (C ₁)	113.0
2	1	2 (B ₂)	2 (C ₂)	110.3
3	1	3 (B ₃)	3 (C ₃)	109.4
4	2 (A ₂)	1	3	118.1
5	2	2	1	115.0
6	2	3	2	108.0
7	3 (A ₃)	2	3	110.4
8	3	1	1	111.2
9	3	3	2	104.0
K1	332.7	342.3	339.2	
K2	341.1	335.7	322.3	
K3	325.6	321.4	337.9	
R	15.5	20.9	16.9	
Optimal level	A ₂	B ₁	C ₁	

In summary, for Process 3, the order of importance of factors that influenced T_d was $B > C > A$; the optimal combination was $A_2B_1C_1$, i.e. the dosages of Al_2O_3 , GA and TPDO were 5.1%, 2.3% and 0.9% respectively. Under these conditions, the average value of T_d from three parallel tests was $118.8 \pm 0.3^\circ C$. For Process 4, the order of importance of factors that influenced T_d was $C > B > A$; the optimal combination was $A_2B_2C_3$, i.e. the dosages of Fe_2O_3 , GA and TPDO were 8.0%, 2.9% and 1.7% respectively. Under these conditions, the average value of T_d from three parallel tests was

Table III **$L_9(3^3)$ experiment parameters and results for process 4.**

Level	Factor (mass percentage based on pickled sheep pelt)		
	A (Fe_2O_3)	B (GA)	C (TPDO)
1	6.0% (A_1)	2.3% (B_1)	0.9% (C_1)
2	8.0% (A_2)	2.9% (B_2)	1.1% (C_2)
3	10.0% (A_3)	3.1% (B_3)	1.7% (C_3)

Test Number	A (Fe_2O_3)	B (GA)	C (TPDO)	T_d ($^\circ C$)
1	1 (A_1)	1 (B_1)	1 (C_1)	104.4
2	1	2 (B_2)	2 (C_2)	111.8
3	1	3 (B_3)	3 (C_3)	110.7
4	2 (A_2)	1	3	115.1
5	2	2	1	113.4
6	2	3	2	109.5
7	3 (A_3)	2	3	114.0
8	3	1	1	105.1
9	3	3	2	108.1
K1	326.9	324.6	322.9	
K2	338.0	339.2	329.4	
K3	327.2	328.3	339.8	
R	11.1	14.6	16.9	
Optimal level	A_2	B_2	C_3	

$116.1 \pm 0.7^\circ C$. For Process 5, the order of importance of factors that influenced T_d was $B > C > A$; the optimal combination was $A_2B_3C_2$, i.e. the dosages of Fe_2O_3 , GA and TPDO were 8.0%, 3.1% and 1.1% respectively. Under these conditions, the average value of T_d from three parallel tests was $110.1 \pm 0.8^\circ C$.

Comparison of Tanning-dyeing Effect of the Five Processes

The hypothesis mechanisms for processes 1-5 are illustrated in Figure 7 - 9. In Figure 8 and Figure 9, "M", may be a mono-

Table IV **$L_9(3^3)$ experiment parameters and results for Process 5.**

Level	Factor (mass percentage based on pickled sheep pelt)		
	A (Fe_2O_3)	B (GA)	C (TPDO)
1	6.0% (A_1)	2.3% (B_1)	0.9% (C_1)
2	8.0% (A_2)	2.9% (B_2)	1.1% (C_2)
3	10.0% (A_3)	3.1% (B_3)	1.7% (C_3)

Test Number	A (Fe_2O_3)	B (GA)	C (TPDO)	T_d ($^\circ C$)
1	1 (A_1)	1 (B_1)	1 (C_1)	100.0
2	1	2 (B_2)	2 (C_2)	104.3
3	1	3 (B_3)	3 (C_3)	109.1
4	2 (A_2)	1	3	109.5
5	2	2	1	106.1
6	2	3	2	110.0
7	3 (A_3)	2	3	102.0
8	3	1	1	101.2
9	3	3	2	108.1
K1	313.4	310.7	307.3	
K2	325.6	312.4	322.4	
K3	311.3	327.2	320.6	
R	14.3	16.5	15.1	
Optimal level	A_2	B_3	C_2	

metallic complex, di- or multi-metallic complex; and the proposed mechanism in each figure does not include all of the possible mechanisms in each process.

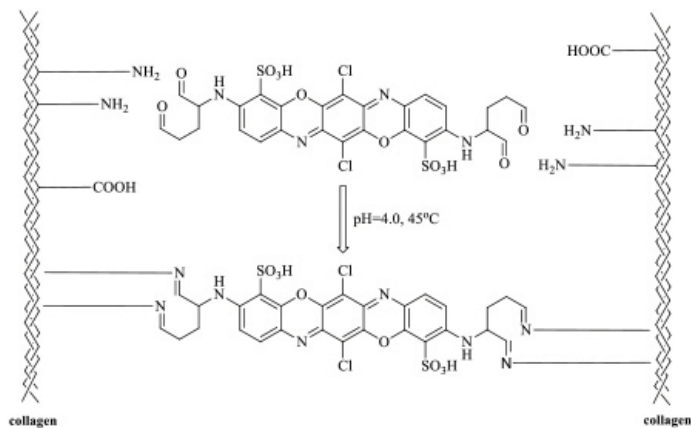


Figure 7. Hypothesis of mechanism for Process 1.

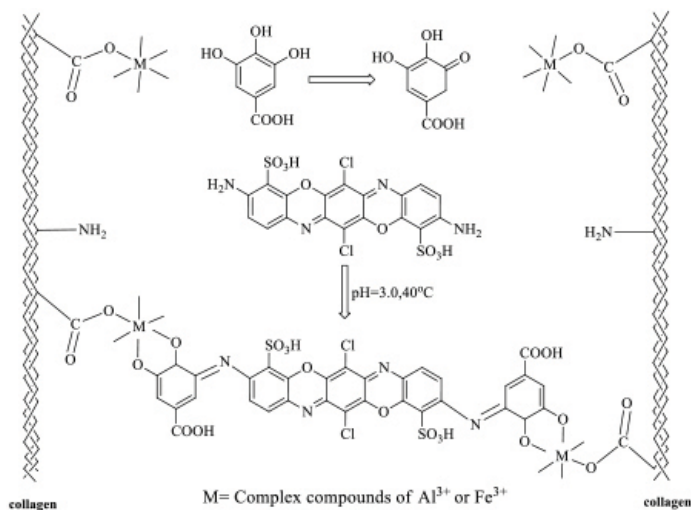


Figure 8. Hypothesis mechanism for Processes 2 and 4.

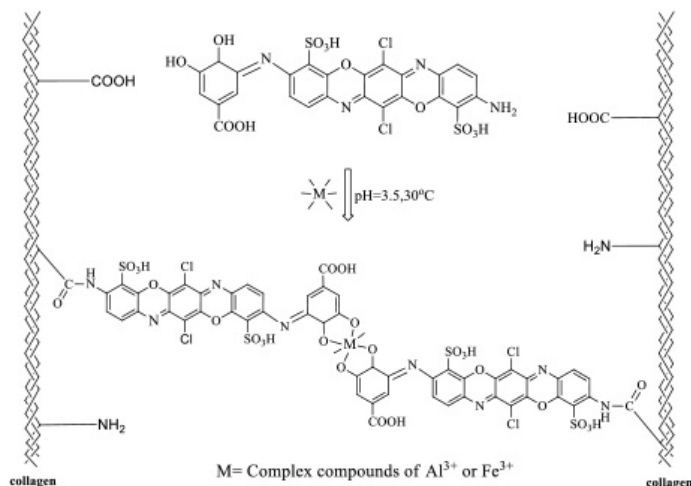


Figure 9. Hypothesis mechanism for Processes 3 and 5.

During Process 1, TPDO-GT, a simultaneous tanning-dyeing material, crosslinks with collagen through a “Schiff-base” reaction, in the same way as a normal aldehyde tanning agent. During Process 2 and Process 4, metallic complex compounds coordinate with the carboxyl groups of collagen, and then, as a bridge, TPDO-GA takes part in coordination, thereby forming cross-linkages. During Process 3 and Process 5, TPDO-GA was

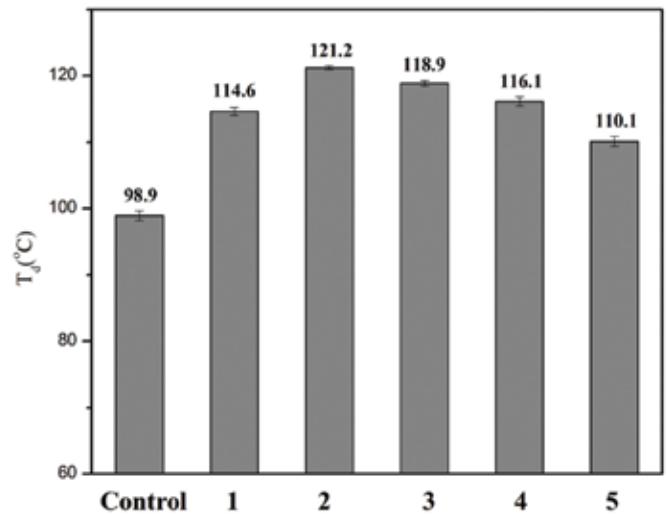


Figure 10. Denaturation temperatures (T_d) of treated pelt from five processes.



Figure 11. Color of the treated pelt from five processes.

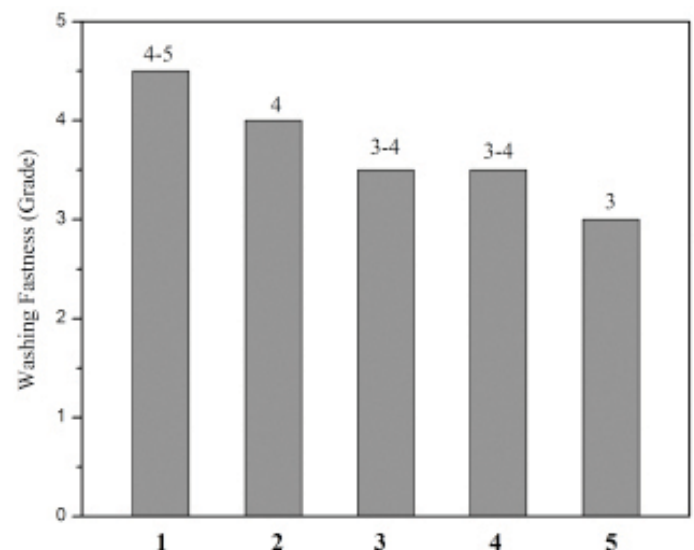


Figure 12. Washing fastness of treated pelt from five processes.

combined with the collagen matrix through amidation with the carboxyl groups of collagen, then they coordinate with metallic complex compounds to form cross-linkages.

The values of T_d of the control sample and the treated pelt from each process is shown in Figure 10. These values were measured using DSC, and the pelt samples were dried at room temperature and room humidity. The magnitudes of T_d were therefore different than those of the shrinkage temperatures (T_s), which were measured in water.

From Figure 10, we calculated that ΔT_d (T_d of treated pelts minus that of control sample) for Processes 2, 3, 4, 1 and 5 were 22.3°C, 20.0°C, 17.2°C, 15.7°C and 11.2°C, respectively. These results indicate that the tanning effect of the combination M (III) + (TPDO+GA) was better than that of (TPDO+GA) + M (III); and the tanning effect of the combination Al (III) with (TPDO+GA) was better than that of Fe (III) with (TPDO+GA). Comparison of ΔT_d of Processes 2, 3, 4 and 1 revealed that the tanning effect of the combination of M (III) with (TPDO+GA) was better than that with TPDO-GT because of the synergistic effect between metallic complexes and polyphenol coordinates.

Colors of the treated pelts from each process are given in Figure 11. The five processes based on TPDO, having the same ingredients but different orders of addition, led to different colors.

Figure 12 indicated that treated pelt from Process 1 possessed the best washing fastness, probably because all of the bonds in the cross-linked structures were covalent bonds (Figure 7). However, the cross-linked structures formed from the other four processes contained coordinate bonds which were more readily broken in water (Figure 8, 9).

Conclusions

(1) The tanning effect of the combination M (III) + (TPDO+GA) was better than that of (TPDO+GA) + M (III); the tanning effect of the combination of Al (III) with (TPDO+GA) was better than that of Fe (III) with (TPDO+GA). The tanning effect of the combination of M (III) with (TPDO+GA) was better than that with TPDO-GT because of the synergistic effect between metallic complexes and polyphenol coordinates.

(2) The five processes based on TPDO, having the same ingredients but different orders of addition, led to different colors. When all of the bonds in the cross-linking structures formed during the treating process were covalent bonds, the treated pelt possessed a better washing fastness.

Acknowledgement

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