

Synthesis and Application of a Novel Cationic Surfactant based on Quaternary Ammonium Salt for Leather Fatliquoring

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Abstract

A fatliquor is an indispensable agent for leather, giving softness, fullness and elasticity. A quaternary ammonium salt cationic surfactant (cetyl-dimethyl-(3-methacrylamide) propyl bromide (DMPC16)) was synthesised from N-(3-dimethylaminopropyl) methacrylamide (DMPMA) and hexadecane bromide by nucleophilic substitution reaction. The structure and properties of quaternary ammonium cationic surfactant were characterised by FTIR, ¹H-NMR, elemental analyser, TGA and surface tension analyser. Further, it was applied in the fatliquoring process of wet-white (Clariant EasyWhiteTan F-90) tanning system to test the physical and mechanical properties, softness, air permeability and absorptivity of the fatliquoring leather. The results showed that quaternary ammonium salt cationic surfactant was successfully prepared, and its surface tension was 31.87mN/m. The application tests showed that the absorption rate of fatliquor reached 97.8%. At the same time, the softness and physical and mechanical properties of the treated leather were improved, including softness increased by 109%, tensile strength increased by 17.2%, tear strength increased by 50.1%, and air permeability increased by 891.21L/(cm²•h). The results showed that quaternary ammonium cationic surfactant had good fatliquoring properties in F-90 tanning system, which can improve the softness, tensile strength and tear strength of leather.

INTRODUCTION

Fatliquoring is a very important process in leather processing.¹⁻³ If the leather is not so treated, the active groups on the tanned collagen fibres will be close to each other and will interact after drying, which will cause the fibres to bond and make the leather hard and dry and it will not meet wear requirements.⁴⁻⁷ Fatliquoring agents used in leather processing can be classified into anionic, cationic, non-ionic and amphoteric fatliquoring agents according to their charge characteristics. Anionic fatliquoring agents are the most widely used, because chrome tanning is still the main method used in leather manufacture. Chrome-tanned leather has strong positive charges and abundant amino groups (-NH₂), which provide the binding point with collagen fibres for anionic fatliquoring agents. However, chrome tanning has a negative effect, regarding the environment and human body, which restricts the sustainable development of leather industry.⁸⁻¹² Therefore, the technology of chrome-free ecological tanning has become a prominent research hotspot in the leather industry. In view of the weak positive charge and lower pl of organic tanned leather, there is an inevitable trend to design and develop cationic fatliquoring agents for organic chrome-free tanning to improve the absorption and binding capacity of traditional wet finishing materials. At the same time, a cationic fatliquoring

agent has antistatic, bactericidal and softness properties they can also be used for secondary fatliquoring, that is to say, used in the later stage of leather dyeing can not only play the role of surface oiling but also fix an anionic fatliquoring agent and anionic dyestuff. At the same time, it is conducive to improving the absorption rate of anionic materials and the oil wettability and further prevent grain brittleness and increase mercerisation of suede leather. In this case, the finished leather also has some anti-mildew effect. A cationic fatliquor may also be used in tanning to reduce the convergence of a tanning liquor and help its penetration and absorption.

Therefore, a cationic fatliquor is an important material for the production of light leathers such as suede leather, garment leather, glove leather and shoe upper leather. At present, there are few studies on cationic fatliquoring agents in China. There are two main methods to synthesise cationic fatliquoring agents. One is the modification of oils. The corresponding cationic surfactant group is introduced into the oil composition. In Western countries these oils are mainly based on petroleum-based chemicals, while in China they mainly based on modification of natural oils which limits the properties of the fatliquor to a certain extent, and a large amount of waste liquor will be produced in the process of modification. The utilisation rate of a fatliquor is low and the waste liquor

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of fatliquor will pollute the environment.¹³⁻¹⁷ The other method is to add cationic surfactants into oil components as emulsifier. The quaternary ammonium salt cationic fatliquor is composed of a quaternary ammonium salt surfactant as the active agent and other neutral oils and auxiliaries. Because the cationic active component in a quaternary ammonium salt fatliquoring agent has good water solubility, acid and alkali resistance, it gives a good performance fatliquor.¹⁸⁻²⁰ In our work a quaternary ammonium salt type surfactant was synthesised from N-(3-dimethylaminopropyl) methacrylamide (DMAPMA) and hexadecane bromide by nucleophilic substitution. It is applied to the F90 Leather fatliquoring process. The physical and mechanical properties, softness, air permeability of the leather and absorptivity of fatliquoring agent were tested. The results show that the fatliquor agent had a good effect. Therefore, in this paper, the synthesised cationic fatliquoring agent not only provides a matching fatliquoring agent for chrome-free ecological tanning, but also reduces the environmental pollution caused by a chrome tanning agent.

1 EXPERIMENTAL SECTION

1.1 Materials

N-(3-dimethylaminopropyl) methacrylamide (purity >99%) and hexadecane bromide (purity >99%) were purchased from Shanghai Maclean Biochemical Technology Co. Ltd. Hydroquinone monomethyl ether (purity >99%) was bought from Shanghai Maclean Biochemical Technology Co. Ltd., acetone was purchased from Tianjin Tianli Chemical Reagent Co. Ltd. and petroleum ether, was purchased from Tianjin Fuyu Fine Chemical Co. Ltd. White-wet leather was purchased from Hebei Dongming Leather Co. Ltd. (F-90) All other reagents are analytically pure and used without purification.

The Vert70 Fourier transform infrared spectrometer and the Advance III 400MHz NMR spectrometer were provided by Brook Company (Germany); Vario EL cube element analyser was provided by the Elementar Company (Germany); The GSD-350 drum was produced by Wuxi Xinda Light Industry Machinery Co. Ltd.; The XK-8012 leather tensile strength testing machine was produced by Kunshan Xiangke Detection Instrument Co. Ltd.; QBZY-1 surface tensiometer was provided Shanghai Fangrui Instrument Co. Ltd. Ultra-depth-of-field microscopy was produced by Beijing Pricey Instruments Co. Ltd.; FEI Q45 Environmental Scanning Electron Microscope (E-SEM), was made by FEI Company (USA).

1.2 Synthesis of quaternary ammonium salt cationic surfactant

1mol N-(3-dimethylaminopropyl) methacrylamide and 0.05 mmol hydroquinone monomethyl ether were added to 27ml acetone solution respectively. 1.2mol 1-bromohexadecane was added slowly at 45°C, and then reacted at 45°C for 22 hours. After precipitation with petroleum ether, the unreacted monomers were removed and then dried in vacuum. Cationic surfactant was obtained. The reaction diagram is shown in Fig. 1.

1.3 Characterisation

1.3.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (Vector-70, Bruker, Germany) was used to characterize the structure of hexadecane bromide, N-[3-(Dimethylamino) propyl] methacrylamide and quaternary ammonium salt cationic surfactant and fatliquor. The scanning frequency ranged from 4000 to 400cm⁻¹.

1.3.2 Nuclear magnetic resonance spectrum (¹H-NMR)

The purified solid samples of 1-bromohexadecane, N-[3-(dimethylaminopropyl) methacrylamide and cationic surfactant were dissolved in DMSO-d₆ and their NMR spectra were obtained by Advance III 400 MHz NMR spectrometer.

1.3.3 Elemental analysis

Appropriate purified samples were examined by the Vario EL III elemental analyser to detect the content of C, H and N elements.

1.3.4 Thermal stability

In a nitrogen atmosphere of 25-600°C, the heating rate was 5°C/min and the nitrogen flow rate was 60mL/min.

1.3.5 Surface tension

The samples were dissolved in pure water and solutes of different quality were added to prepare water solutions of different concentrations. The surface tension of different concentrations was measured by QBZY-1 surface tensiometer at room temperature.

1.3.6 Analysis of leather properties

(1) Determination of physical and mechanical properties: horizontal and vertical samples from different parts of the leather were fixed on the XL-100A tensile testing machine. The tensile strength and tearing strength were tested and the average value was calculated.

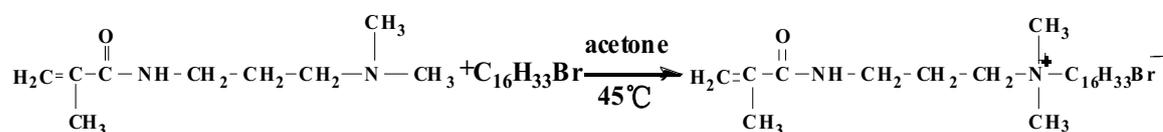


Figure 1. Diagram of synthesis of quaternary ammonium salt cationic surfactant.

(2) SEM observation: The leathers were observed under magnification of x5000 using the Tescan scanning electron microscope (SEM) + energy spectrometer.

(3) Softness: a softness tester was used to test the leather samples following the standard procedures at 25°C. The softness of each sample was measured 3 times, the average results are shown. The softening rate refers to the percentage increase of leather softness before and after fatliquoring. The calculation formula is as follows.

$$T = \frac{d - d_0}{d_0} \times 100\% \quad (1)$$

d – Thickness of leather after fatliquoring (mm),
 d_0 – Thickness of leather before fatliquoring (mm),
 T – The softening rate of Leather (%).

(4) Absorption of fatliquoring agent: The content of fatliquoring agent in the liquor was determined at the start and end of the process by gravimetric method. The absorption of fatliquoring agent was calculated using Eq. (1).

$$\text{Absorption of fatliquoring agent} = (B_1 - B_2) / B_1 \times 100\% \quad (2)$$

Where B_1 was content of fatliquoring agent in initial liquor and B_2 was the content of fatliquoring agent in the waste water at the end of fatliquoring.

(5) Air permeability measurement: The air permeability of leather products is expressed by the air volume per unit area of leather sample that can be permeated per unit time under specified pressure. After air conditioning, the time taken t (s) for 100mL air passing through leather samples with a permeability tester should be less than 0.5 s.

$$K = \frac{100 \times 3600}{10(t - t_0)} = \frac{36000}{t - t_0} \quad (3)$$

K – sample permeability [mL/(cm²•h)];
 t – 100mL air penetration time (s) of leather samples with specified area;
 t_0 – the time needed for blank experiment (s).

1.3.7 Fatliquoring Process

The parameters of the fatliquoring process are shown in Table I.

2 RESULTS AND DISCUSSION

2.1 FTIR analysis

Figure 2 shows the FTIR spectrum of hexadecane bromide, N-[3-(Dimethylamino)propyl]methacrylamide and quaternary ammonium salt cationic surfactants. The absorption peaks at 2921cm⁻¹ and 2853cm⁻¹ in Fig. 2(a)

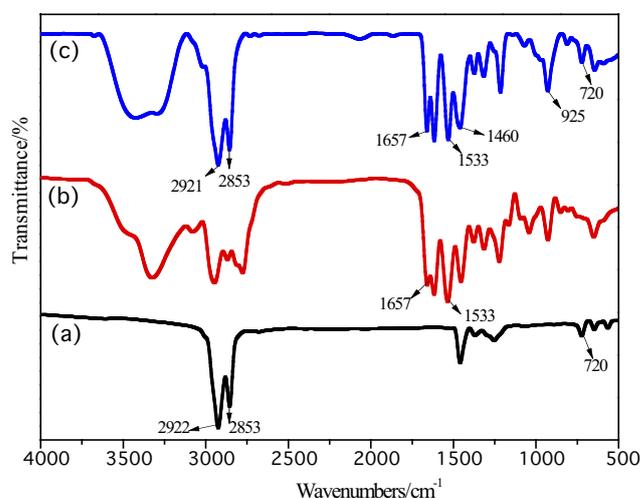


Figure 2. FT-R spectra. (a) Hexadecane bromide, (b) N-[3-(Dimethylamino)propyl]methacrylamide, (c) quaternary ammonium salt cationic surfactant.

TABLE I
Fatliquoring process of wet-white F-90-tanned leather

Process	Chemicals	Dosage (%)	Temperature (°C)	Time (min)	pH	Remarks
Raw material – F-90-tanned sheep white-wet leather						
Degreasing	Water	200				
	Degreaser	1				
Washing	Water	300	37	10		Wash two times
Neutralizing	Water	100	37			
	Neutralising agent	2				
	Sodium formate	1		40		
	Sodium bicarbonate	0.2		40	4.8	
Washing	Water	300	55			
Retanning/fatliquoring	Water	150	50			
	BA tanning extract	6		360		Vegetable tannin
	Fatliquoring	8				O : QASCS = 2:1
	Formic acid	1.2		20	3.5	
Washing	Water	300	27	5		
Hang drying						
O : QASCS = 2:1 , O is oil , QASCS is quaternary ammonium salt cationic surfactant						

indicate the asymmetric and symmetric stretching vibration of methylene and the absorption peak at 720cm^{-1} corresponds to in-plane oscillating vibration absorption peak of long chain alkyl $-\text{CH}_2$. The absorption peak at 1617cm^{-1} in Fig. 2(b) indicates the stretching vibration absorption peak of unsaturated carbon-carbon bond. In in Fig. 2(c), the $\text{C}=\text{O}$ characteristic peak of amide is 1657cm^{-1} , and the stretching vibration characteristic peak of carbon-carbon double bond is 1617cm^{-1} , which proves the existence of double bond in the product. The absorption peaks at 2921cm^{-1} and 2853cm^{-1} of curve (c) indicate the asymmetric and symmetric stretching vibration of methylene, indicating the structural characteristics of trialkylmethyl cations; 720cm^{-1} was the in-plane oscillation absorption peak of long chain alkyl $-\text{CH}_2$; 1460cm^{-1} and 925cm^{-1} were the stretching vibration peaks of C-N in quaternary ammonium groups. This shows the synthesis of quaternary ammonium cationic surfactant.

2.2 $^1\text{H-NMR}$ analysis

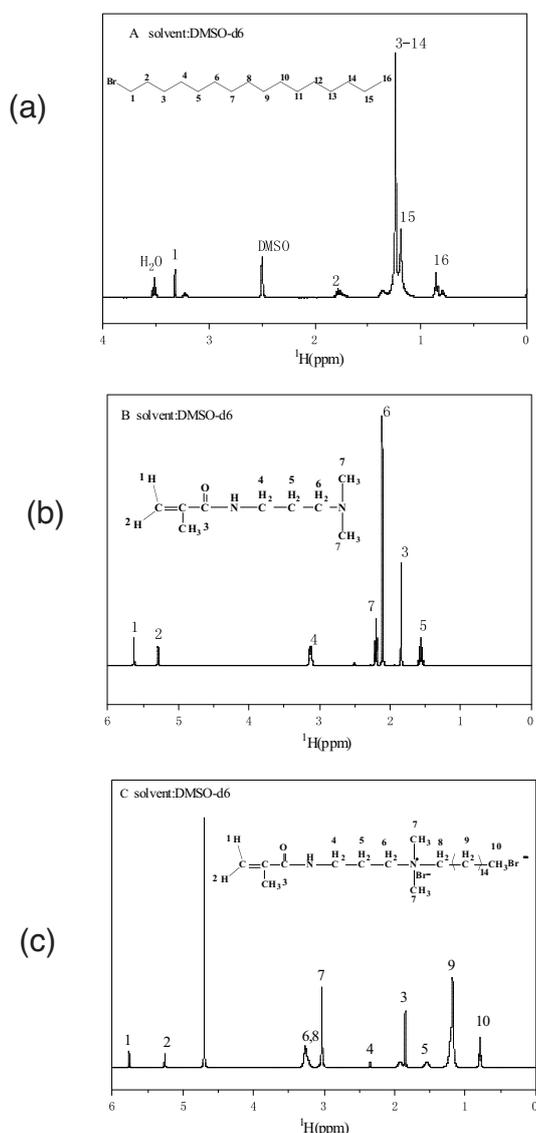


Figure 3. $^1\text{H-NMR}$ spectra. (a) Hexadecane bromide, (b) N-[3-(Dimethylamino)propyl]methacrylamide, (c) quaternary ammonium salt cationic surfactant.

Figure 3. shows the $^1\text{H-NMR}$ spectra of Hexadecane bromide, N-[3-(Dimethylamino)propyl]methacrylamide and quaternary ammonium salt cationic surfactants. It can be seen from Fig. 3(a) that the chemical shift of the end CH_3 is 0.84ppm and that of CH_2 in long alkyl chain is 1.19-1.24ppm. From Fig. 3(b), we can see that the proton chemical shift of $-\text{N}(\text{CH}_3)_2$ is 2.3ppm and Fig. 3(c) also shows that the chemical shift of CH_3 linked to carbon atoms on double bonds is 1.84ppm in the NMR spectra of quaternary ammonium cationic surfactants, and due to its influence, the chemical shifts of two H atoms connected to double bonds are different, appearing at 5.2ppm and 5.7ppm, respectively. Two CH_2 connected with N atom of quaternary ammonium salt are at the chemical shift of 3.2ppm and two CH_3 connected with N atom of quaternary ammonium salt are at the chemical shift of 3.0ppm. The chemical shift of CH_2 in long alkyl chain is 1.54ppm, and the chemical shift of end CH_3 is 0.8ppm. The proton chemical shift of dimethylaminopropyl methacrylamide- $\text{N}(\text{CH}_3)_2$ is 2.3ppm, but the chemical shift of the two CH_3 atoms connected with the quaternary ammonium salt N atom in the synthesised cationic surfactant is 3.0ppm, which proves the synthesis of quaternary ammonium cationic surfactants.

2.3 Elemental analysis

The elemental analysis results of quaternary ammonium salt cationic surfactant are shown in Table II.

Item	C%	N%	H%
Measured value	63.14	5.81%	10.75
Theoretical value	63.11	5.89%	10.8%

Table II shows that the synthesised quaternary ammonium cationic surfactants contain C, H and N elements, in which the content of C is 63.14%, the percentage content of N is 5.81%, and the content of N is 10.75%. The values of C, H and N elements are basically consistent with the theoretical values. Through the above elemental analysis and characterisation, it is shown that the synthesised quaternary ammonium cationic surfactant made under the above experimental conditions is in good agreement with its theoretical structure, and that the expected product is obtained.

2.4 Thermal stability

Figure 4 shows the TGA-DTG curve of quaternary ammonium cationic surfactants it shows that the quaternary ammonium cationic surfactant has a little weight loss before 205°C , about 7%. This may be due to residual solvent or water absorption in the quaternary ammonium surfactant. Its initial decomposition temperature is 210°C , and its decomposition process is divided into two stages. The first stage starts from 210°C to 337°C , the weight loss is about 87%, which

may be caused by the thermal decomposition of quaternary ammonium surfactants. In the second stage, the weight loss is about 4% from 337°C to 461°C, which may be caused by carbon residues, indicating that quaternary ammonium cationic surfactants have certain thermal stability. In conclusion, the synthesised surfactants can be used in leather processing.

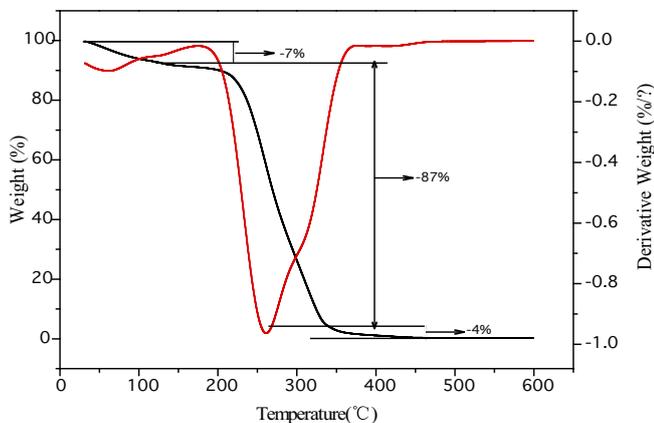


Figure 4. TGA-DTG curve of the synthesised quaternary ammonium cationic surfactant.

2.5 Surface tension

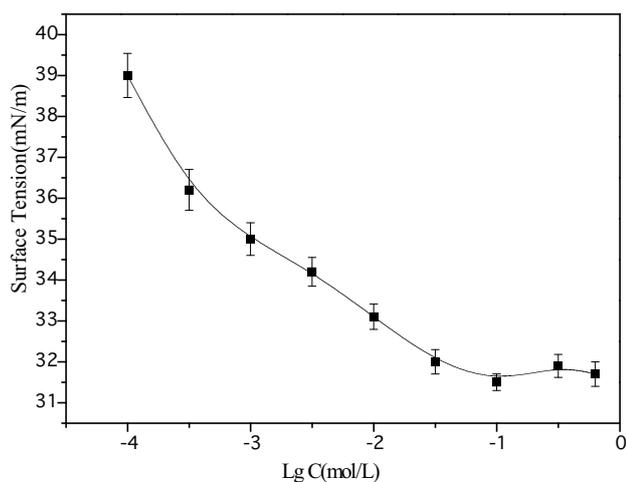


Figure 5. Surface Tension curve of the synthesised quaternary ammonium cationic surfactant.

Figure 5 shows the relationship between the concentration and surface tension of quaternary ammonium cationic surfactants. It can be seen that the surface tension of the solution decreases with the increase of the concentration of the solution. After reaching a certain concentration, the surface tension tends to be stable. At this time, the concentration is the critical micelle concentration (CMC)²¹. The minimum surface tension of 0.1 mol/L quaternary ammonium cationic surfactant solution is 31.8 mN/m. The decrease of surface tension is due to the increase of adsorption of surfactant molecules at the air-water interface.²² Surfactant molecules are adsorbed on the air-water interface, hydrophobic carbon chains are oriented towards air and hydrophilic groups towards

water phase. The concentration of surfactant molecules at the interface increases with the increase of the volume concentration of surfactant, but after reaching CMC, the adsorption capacity of surfactant molecules on the surface does not increase further, and the surface is densely filled with surfactant molecules.²³ At this time, the surface tension will not change with further increase of surfactant concentration.

2.6 Application of quaternary ammonium surfactant in fatliquoring of leather

(1) Leather infrared analysis

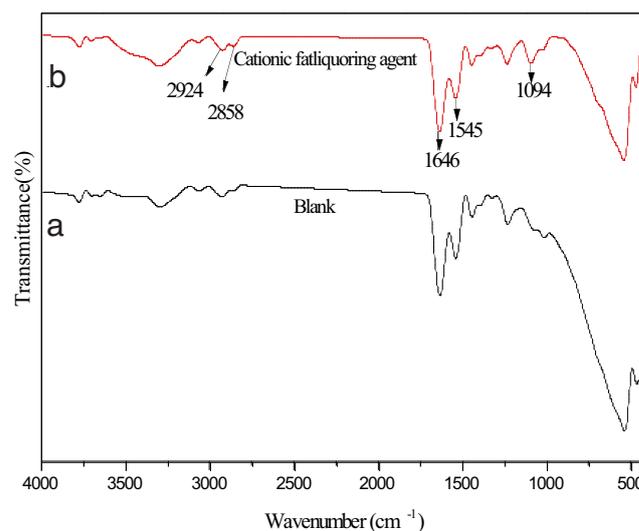


Figure 6. FTIR spectra of leathers. Showing the blank (a) and the synthesised cationic salt fatliquored leather (b).

The structure of leather samples before and after fatliquoring was characterised by infrared diffuse reflectance (ATR accessories). Figure 6 is the ATR-IR diagram of the leather sample after fatliquoring it can be seen from the figure that there is no great fluctuation after fatliquoring, indicating that the addition of cationic fatliquoring agent does not affect the structure of collagen fibril peptide chain. The characteristic absorption peaks at 2924 cm⁻¹ and 2858 cm⁻¹ belong to -CH₃ and -CH₂-, C=C characteristic absorption peaks at 1646 cm⁻¹ and N-H bending vibration at 1545 cm⁻¹. However, due to the introduction of cationic fatliquor there is a stretching vibration peak containing CH₂-N⁺(CH₃)₃ at 1094 cm⁻¹, which indicates that the cationic fatliquoring agent penetrates into leather and does not destroy the conformation of collagen fibres.

(2) Performance testing and analysis of leather

Table III shows the results of air permeability, softness level and absorbency of the leather before and after fatliquoring, it can be seen that the softness of leather treated with the synthesised cationic fatliquor agent and a commodity cationic fatliquor has been improved. Compared with unfatliquored leather, the softness of leather treated with cationic fatliquoring agent and the commercial cationic fatliquor has been increased by 109% and 99% respectively. According to

TABLE III Test results of fatliquoring effect of crust leather				
Crust leathers	Test project			
	Fatliquoring agent absorptivity (%)	Softening rate (%)	Air permeability [mL/(cm ² •h)]	Softness (mm)
Blank	—	—	1002.9	3.92
Cationic fatliquoring agent	97.8	109	891.21	8.2
Commodity	95.9	99	514.41	7.8

the absorption rate of fatliquoring agent, the synthesised cationic fatliquor is little different from the commercial fatliquor. The absorption rate of synthesised cationic fatliquoring agent is 97.8%, and that of commercial agent is 95.9%. The results showed that the air permeability of fatliquored leather decreased. The air permeability of leather treated with the synthetic cationic fatliquoring agent and marketable fatliquoring agent decreased by 111.69ml/cm²•h and 488.49ml/cm²•h, respectively. This may be due to the blockage of the voids by the fatliquoring agent and the resultant decrease of the air permeability.

Test results of physical properties of crust leather

TABLE IV Test results of physical properties of crust leather			
Parameters	Samples		
	Blank	Cationic fatliquoring agent	Commodity fatliquor
Tear strength(N/mm ²)	27.45	32.18	29.43
Tensile strength (N/mm ²)	26.07	39.13	32.86

Table IV shows the results of physical and mechanical properties of fatliquored leather. As we can see, the tensile strength and tear strength of fatliquored leather are obviously higher than those of unfatliquored leather, which proves that the prepared products can improve the physical properties of crust leather. The tear strength and tensile strength of leather treated with the synthesised cationic agent were 4.73N/mm² and 13.06N/mm² higher than those of blank sample, respectively. The relevant values for leather treated with the commercial cationic agent were 1.98N/mm² and 6.79N/mm² higher than those of blank sample, respectively. The results showed that the synthetic fatliquoring agent had the function of isolation and lubrication after it was added into the leather, thus improving the mechanical properties of leather and making the finished leather tougher.

(3) SEM observations

Figure 7 shows the SEM images of leather both with and without cationic fatliquor treatment under the same technological conditions. It can be clearly seen from the images that the collagen fibre bundles of unfatliquored leather are arranged tightly, while the distance between

adjacent collagen fibres treated with the synthesised cationic fatliquor has increased, the degree of looseness of the fibres has increased, and the degree of disorder of fibre bundles has also increased. This is attributed to the synthesised cationic fatliquoring agent structure containing N⁺ ions, which can combine with the carboxyl groups of collagen fibres in the form of ionic bonds. At the same time the cationic fatliquor contains long flexible chains with a lubricating effect which adhere to the surface of the fibre thus reducing the interaction force between the fibres, and increasing their relative mobility and increasing the looseness of the fibres.

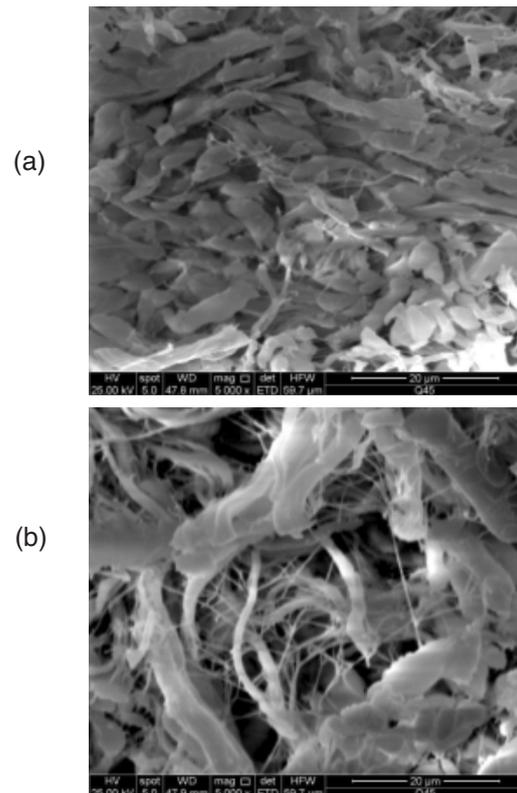


Figure 7. SEM photographs of leather sections. Unfatliquored (a) and the synthesised cationic fatliquored leather (b) (×5000).

(4) Ultra-depth microscope photos of leather

The roughness of the leather grain and the size of leather pores are important indexes affecting the handle of leather. Figures 8 (a) and (b) present grain Ultra-depth microscope photos of unfatliquored and

synthesised cationic fatliquored leather, respectively. As can be seen from Fig. 8(a), the grain surface of the unfatliquored leather is flat and rough, the pores of leather are small and plentiful, whilst the grain surface of the fatliquored leather is smooth, and the pores of the leather are larger and fewer. This is because the fatliquoring agent containing grease/oil penetrates into the fibres of the leather, which blocks the voids of leather and reduces the number of voids. At the same time, the flexible long chains with lubrication properties in the structure of cationic fatliquoring agent can increase the distance between the collagen fibre bundles, which makes the collagen fibres aggregate in a disorderly manner, increases the looseness of the leather and enlarges the pore sizes.

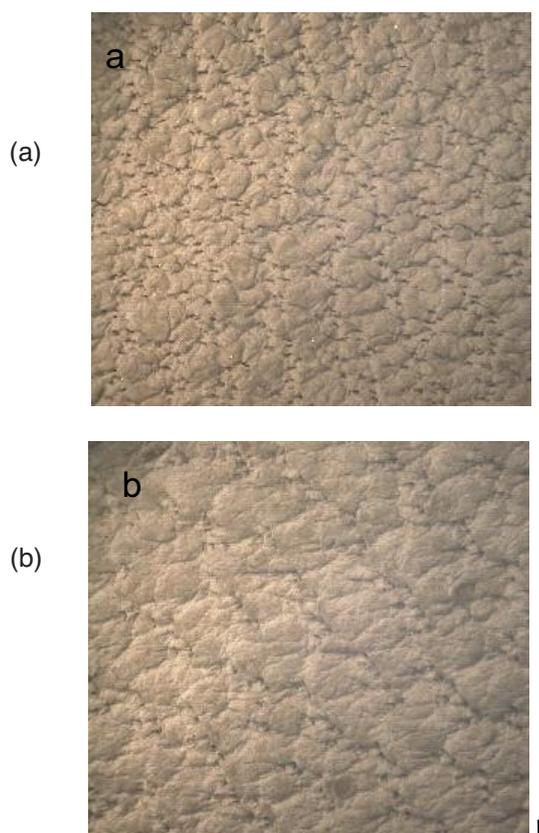


Figure 8. Ultra-depth microscope photos of unfatliquored leather (a) and fatliquored leather (b) (×50).

3 CONCLUSIONS

A quaternary ammonium salt cationic surfactant was synthesised from N-(3-dimethylaminopropyl) methacrylamide (DMAPMA) and hexadecane bromide by nucleophilic substitution reaction. The results showed that the quaternary ammonium salt surfactant had good surface activity, and its surface tension was 31.87mN/m. It was applied to the fatliquoring of the wet-white (F-90) tanning system. The results indicated that there was a certain physical and chemical interaction between the treated leather and collagen fibres, and the softness and physical and mechanical properties of the treated leather were improved. The softness, tear strength, tensile strength and absorption

of fatliquor were increased by 109%, 50.1%, 17.2% and 97.8% respectively. The air permeability was 891.21L/(cm²•h)]. The results showed that the quaternary ammonium cationic surfactant had good fatliquoring properties in the wet-white leather (F-90) tanning system.

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