Preparation of Fatliquoring-retanning agent with a reinforcing effect by free-soap microemulsion conpolymerization

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Abstract: The optimal synthesis conditions of reactive emulsifier were optimized via orthogonal test, then retanning agent with a reinforcing effect was prepared by microemulsion conpolymerization. The potassium salt of maleic anhydride lauryl alcohol monoester which was a kind of reactive emulsifier was prepared. Substituting lauryl sodium sulfate for the reactive emulsifier, the fatliquoring-retanning agent with a reinforcing effect was synthesized by free-soap microemulsion copolymerization. The pigskin splits were retanned by the fatliquoring-retanning agent. The results showed that when the ratio of reactive emulsifier and mixed monomer was equal to 1:4, the total weight was 30g(the dosage of n-butyl arcylate was 50%, the dosage of methyl methacrylate was 41.7% and the dosage of cross-linking was 8.3%), and the dosage of acrylic acid was 1.0%, the retanning effect was best. The tear strength of cross direction was improved by 61.34%, while the length direction was improved by 37.92% so that the properties of leather can be improved integrally, which was beneficial to deep-processing of the leather. Besides, burst strength was improved by 53.18%.

Keywords: soap-free, microemulsion conpolymerization, acrylic resin, fatliquoring-retanning agent

1 Introduction

Nowadays the leather is demanded more soft, which in a certain extent influences physical-mechanical properties and durability of leather. So one production that can not only improve physical-mechanical properties of leather but also benefits to leather's softness need to be researched. Fatliquoring-retanning agent with a reinforcing effect belongs to the production. Retanning agent with a reinforcing effect by microemulsion conpolymerization has been studied and acrylic resin nanometer emulsion of solid content 25% is prepared by semi-continuous feeding(the average grainsize is 20nm).The pigskin splits are retanned by it, which can improve the leather's tensile strength grately[1-3]. The combing force of its carboxy groups and chromium in chrome tanned leather is strong and stable, and it can't move to the surface of leather to form spew. As a result, the leather retanned takes on persist softness and dye cleanability. The grainsize of fatliquoring-retanning agent synthesized by soap-free microemulsion copolymerization is among the size of nanometer, on the surface of which has carboxyl groups and can make collagens or peptide chain away from decades of namometers cross link, so that the intensity and the compactness of the leather are improved[4-6]. In the meantime, because the polymer's lateral chain had lubricant groups, the strength of the leather is improved and the suppleness has no negative effect.

At present time, the application of reactive emulsifier in microemulsion is gradually becoming a hot topic[7-9]. The emulsifier molecule can permanently copolymerize with monomer and effectively advance latex property. The reactive emulsifier-potassium salt of maleic anhydride lauryl alcohol monoester was prepared. Completely substituting lauryl sodium sulfate for the reactive emulsifier, the fatliquoring-retanning agent via free-soap microemulsion copolymerization was synthesized, and it was applied in the retanning process, the effect was good.

2 Experimental section

2.1 Materials and apparatus

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maleic anhydride(MAH), made in Six chemical reagent factory of Tianjin; lauryl alcohol(LA), made in Tiantai fine chemical company of Tianjin; crylic acid(AA) was made in Hongyan chemical reagent factory of Hedong zone, Tianjin; n-butyl acrylate (BA), made in Xudong chemical reagent factory of Beijing; methyl methacrylate (MMA), made in Shanghai chemical reagent factory of China medicine company; divinylbenzene (DVB), made in Fluka of Switzerland; ammonium persulfate(ASP), made in Six chemical reagent factory of Tianjin; n-amyl alcohol(PA), made in Purchasing and supply station of Shanghai chemical reagent factory ; ART-1,acrylic acid retanning agent made in China; Tannit LSW, soft agent with reinforcing effect made in Böhme Company of Germany; sample skin, chrome-tanned pigskin splits as garment leather made in China.

Vector22 IR spectrum machine made in Bruker Company of Germany; TS-2000-S multi-functional material testing machine made in Gaotie Ltd of Taiwan.

2.2 preparation of reactive emulsifier

The reactive condition was determined via orthogonal test on the base of information reported[10]. After preparing maleic anhydride lauryl alcohol monoester, it was neutralized by using 20% potassium salt solution.

2.3 preparation of free-soap microemulsion

n(mixed monomer):n(potassium salt of maleic anhydride lauryl alcohol monoester) was respectively 5:1,4:1,3:1and 2:1. The potassium salt of maleic anhydride lauryl alcohol monoester was firstly dissolved in three-necked flask, then 1mL PA was added. After temperature was raised to 75℃, 3mL mixed monomer (m(MMA):m(BA)=1:1) and 0.36g ASP were added, then reacted 30min. The mixed monomer was continued to be slowly dripped at the rate of 0.004mL/s. The whole reaction was about 4h, after which the reaction was still kept on 1.5h at 80℃.

2.4 Retanning process of leather

Neutralization

water	150%	35℃		
sodium hydrogen carbonate	0.8%			
sodium acetate	1.0%			
			3×15min+40min	pH 5.5

retan

water	200%	35℃		
penetrating agent H-900	0.2%			
microemulsion fatliquoring-retanning agent (calculated by solid content)	2%			
(the using methods of Tannit LSW and ART-1 are the same to microemulsion)				
		3×10min+90min		wash

Dyeing and fatliquoring

water	200%	65℃		
castor oil sulfonate	12%		60min	
dyestuff	2%		10min	
formate	1.2%		30min	pH 3.6

2.5 Testing of physical-mechanism properties of leather

Basing on the standard of garment leather, we test the tensile strength, tear strength and burst strength in multi-functional material testing machine[11].

3 Results and dicussion

3.1 optimal reaction conditions of reactive emulsifier

The percent conversion of lauryl alcohol must be increased because its lateral chain had lubricant groups which had negative effect on the water-solubility of polymerized surfactant.

Table 1 The results of the orthogonal test

Experimental Number		levels			Percent Conversion of LA (%)	Residues of MAH in Products(%)
		A Ratio of MAH and LA	B Temperature(℃)	C Time(h)		
1		1	1	1	96	1.97
2		1	2	2	97	1.77
3		1	3	3	99	0.92
4		2	1	2	100	1.24
5		2	2	3	100	1.36
6		2	3	1	100	1.38
7		3	1	3	100	1.33
8		3	2	1	100	2.81
9		3	3	2	100	1.43
Percent conversion of LA	K_1	292	296	296	∑=892	
	K_2	300	297	297		
	K_3	300	299	299		
	k_1	97.33	98.67	98.67		
	k_2	100	99	99		
	k_3	100	99.67	99.67		
	Rj	2.67	1.00	1.00		
Residues of MAH in Products	K'_1	4.655	4.545	3.777	∑=14.208	
	K'_2	3.979	5.935	2.144		
	K'_3	5.574	3.728	3.609		
	k'_1	1.552	1.515	1.259		
	k'_2	1.326	1.978	1.418		
	k'_3	1.858	1.243	1.203		
	R'_j	0.532	0.735	0.215		

The results showed that when mol ratio of MAH and LA was from 1.05 to 1.15, the conversion of lauryl alcohol was nearly complete. When temperature changed from 80℃ to 90℃, the percent conversion of lauryl alcohol increased 1% and the residue of maleic anhydride was not influenced obviously, but in order to inhibit the synthesis of dibasic acid esters, so 80℃was chose. Besides, the reaction time was not important factor, so we chose 3h as the appropriate time. In a word, the optimal condition of esterification reaction of maleic anhydride and lauryl alcohol was: 80℃, 3h, n(MAH):n(LA)=1.15.

3.2 Characterization of reactive emulsifier

In IR spectra of maleic anhydride lauryl alcohol monoester, there was no narrow peak of 3300 cm^{-1} which showed there are no hydroxyl groups in the sample, that is to say, the lauryl alcohol had reacted completely. The peak of 1059cm^{-1} and 1217cm^{-1} showed that there was ester. The broad peak of 3000-2500cm^{-1} showed there were carboxyl groups. So we knew that the maleic anhydride lauryl alcohol monoester had been prepared.

3.3 Effects of solid content 30% on leather's properties

The retanning agent with reinforcing effect researched previously in our Laboratory can make tensile strength increase 68% and tearing strength increase 44%, which was better than microemulsion fatliquoring-retanning agent prepared now in this test. Trying to increase the solid content to 30%, so that the diameter of particles was larger and the bonding points of groups and Cr3+ was more than before, which could make the reinforcing effect more obvious.

The ratio of reactive emulsifier and mixed monomer was fixed in 1:4, and their weight was simultaneously increased till their total weight was 30g(the dosage of butyl acrylate was 50%,the of dosage of methyl methacrylate was 41.7% and the dosage of cross-linker was 8.3%), the dosage of acrylic acid which was hydrophilic monomer was 1.0%. The pigskin splits were retanned by the fatliquoring-retanning agent. The effects of leather was as follows:

Table 2 The increased percentage of properties of leather

type	Thickness Variety (%)	Tear strength (%)		Tensile strength(%)		Burst strength (%)
		cross direction	length direction	cross direction	length direction	
microemulsion	13.02	61.34	37.92	29.37	12.28	53.18

The Tear strength of cross direction could be improved by 61.34% and the length direction could be improved by 37.92%, so that the property of leather was improved more than before, which was beneficial to deep-processing of the garment. Besides, the softness of the retanned leather was the same with the leather that was not retanned by the fatliquoring-retanning agent and the handle is all right. From the table we also know that burst strength was improved by 53.18% which was benefit for the shoe-making.

3.4 Comparison test with Tannit LSW and ART-1

Tannit LSW is a special supple agent which can not only keep leather's suppleness, but also increase leather's tear strength, and its basic composition is sulfate fatty alcohol derivatives, anion. And ART-1 is a retanning agent which can increase leather's thickness and tensile strength, and its basic composition is acrylic resin, anion. Comparing with the two products, we confirm that the reinforcing effect on leather of fatliquoring-retanning agent.

Table 3 Contrast of suppleness

suppleness	Score
Blank sample	3.5
fatliquoring-retanning agent	4
Tannit LSW	4.5
ART-1	2

Table 4 The increased percentage of properties of leather

type	Thickness variety(%)	Tensile strength(%)		Tear strength(%)		Burst strength(%)
		cross direction	length direction	cross direction	length direction	
ART-1	12.20	45.86	9.93	-43.79	-38.71	8.90
LSW	2.30	3.54	16.23	4.57	7.18	7.40

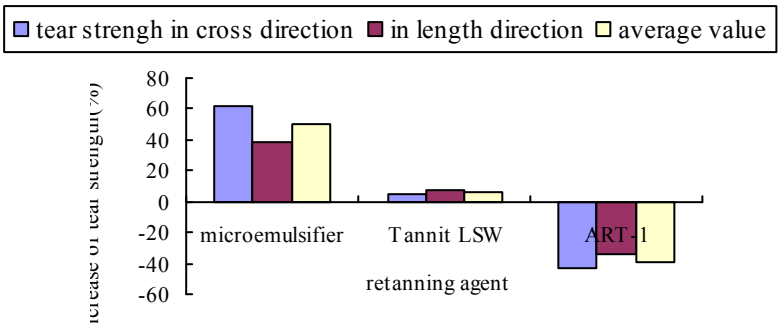

Fig.1 Effects on tear strength by type retanning agent

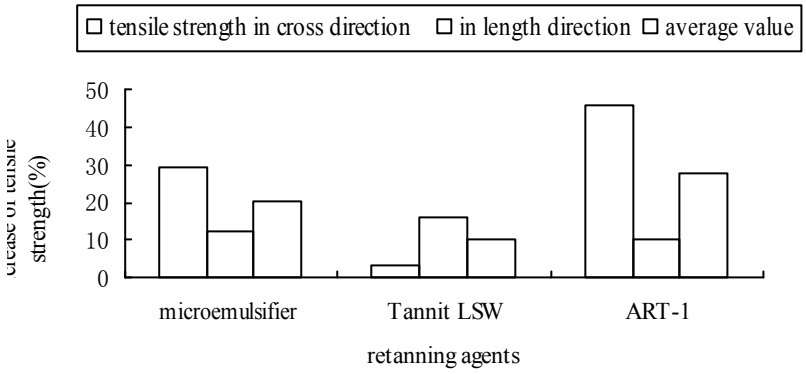

Fig.2 Effects on tensile strength by type of retanning agent

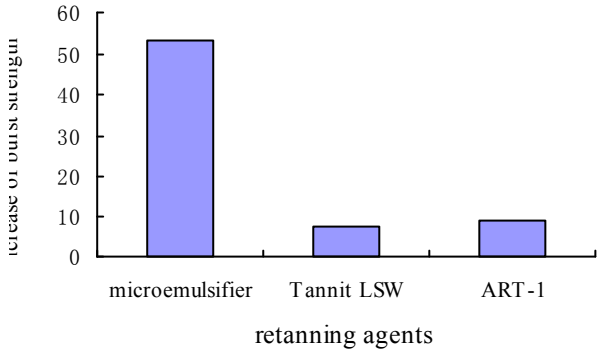

Fig.3 Effects on burst strength by type of retanning agent

As shown in Fig.1, 2, 3 and 4, the tear strength enhanced by fatliquoring-retanning agent was more than ART-1 and of Tannit LSW, the tensile strength enhanced by ART-1 was little better than fatliquoring-retanning agent and Tannit LSW, and the burst strength was improved 53.18% by fatliquoring-retanning agent while 7.40% by Tannit LSW and 8.92% by ART-1.The effects of the three products on tensile strength in length direction is the same, while in cross direction ART-1 is better than microemulsive fatliquoring-retanning agent. Besides, the suppleness of leather was also satisfied. Considering all kinds of performance indexes, we see that the general properties of acrylic resin fatliquoring-retanning agent synthesized by soap-free microemulsion copolymerization were more excellent than Tannit LSW and ART-1.

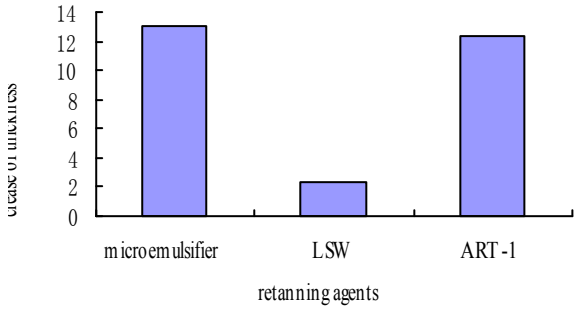

Fig.4 Effects on increasing thickness by type of retanning agent

4 Conclusions

Through orthogonal test we got the optimal conditions of esterification reaction of maleic anhydride and lauryl alcohol which was 80℃,3h,n(MAH):n(LA)=1.05.

According to the procedure the optimal ratio of materials is got. The ratio of reactive emulsifier and mixed monomer was fixed in 1:4, and their weight was simultaneously increased till their total weight was 30g(the dosage of butyl acrylate was 50%,the of dosage of methyl methacrylate was 41.7% and the dosage of cross-linker was 8.3%), the dosage of acrylic acid which is hydrophilic monomer was 1.0%. The retanning effect was best.

The application results showed that the tear strength of cross direction was improved by 61.34%, while the length direction was improved by 37.92%, so that finally the tear strength in cross direction and length direction was tend to be the same. Meantime, the tensile strength was improved by 26.36% and burst strength was improved by 53.18%.

The results of comparison test with Tannit LSW and ART-1 showed that the tear and the tensile strength of cross direction were improved by61.34% and 29.37% that is better than Tannit LSW and ART-1 in retanning pigskin splits. In length direction, the three productions have the same effect. The burst strength was improved by 53.18%.The general properties of leather tanned by acrylic resin retanning-fatliquoring agent which was synthesized via free-soap microemulsion copolymerization were all more excellent than by Tannit LSW and ART-1.

Acknowledgments

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References

[1] Wang Xuechuan,An Huarui Sun Ming, Luo Yanhong, Feng Jianyan, ,JSLTC. 2005.89 (4)

[2]Wang Xuechuan, Sun Ming, An Huarui, Feng Jianyan. China Leather,2005,34(1):39 -41

[3]Xu Xiangling, Yin Yadong, Ge Xuewu,etal. Chemical Journal of Chinese Universities, 1999,20(3):478-485

[4]Ke Changmei, Wang Houzhi, Duan Hui, etal. Advances in Fine Petrochemicals, 2003,4(6):11-16

[5]Liu Yi, ZhangLi, Liu Jingqin, etal. Fine Chemicals, 2002,19(12):729-731

[6]Gong Tao, Lu Deping, Guan Rong. Chinese Journal of Colloid & Polymer, 2003,21(3):27-30

[7]You Lisha, Fu Zhong, Wu Huaqiang. Chinese Journal of Chemical Physics, 2001,14(4):474-478

[8]G.Mallikarjun,P.Saravanan. JALCA,2002,97:215-224

[9]Wan Bo,Wang Dening. China Synthetic Rubber Industry,2003,26(2):94-97

[10]Jiang Weiqi. Beijing:Publishing Company of light industry in China, 1999.

[11]Wang Xuechuan,Sun Ming,An Huarui,etal. Fine Chemicals,2005,22(6):464-467.