Synthesis of Amphoteric Phosphate Ester Fatliquor by Polyphosphoric Acid and Its Application in Free-chrome tanning

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Abstract: Taking polyphosphate as the phosphorylated reagent, amphoteric phosphate fatliquor was prepared. And it was applied in the fatliquor of metal–free tanned leather. The optimum reaction condition was obtained through optimized experiment: molar ratio of hydroxyl and P205 was 3.0:1.0, reaction temperature was 80℃, and reaction time was 5.5h. Under the optimum condition, content of MAP was 89.30% in the phosphate and conversion ratio of P205 was 97.20%. Through the research and application test of the amphoteric phosphate fatliquor, the result indicated that the fatliquor could be applied in the fatliquor of metal–free tanned leather.

Key words: Polyphosphoric acid, amphoteric phosphate, metal–free tanned leather

1 Introduction

The phosphate ester which is an important surfactant is widely used in many fields, such as chemical fiber, spinning and weaving, plastic, papermaking and daily chemical products. The basic synthesis mechanism of phosphate ester is the esterification reaction, during which the material containing hydroxyl groups and phosphorylated reagent are used, but the concrete way of phosphorylation reaction is different from each other. At present the main phosphorylated reagent are phsophorus pentoxide, phosphorus trichloride, phosphorusoxychloride, polyphosphoric acid and so on [1-5]. In this paper, polyphosphoric acid is selected as phosphorylated reagent to prepare amphoteric phosphate fatliquor, in which the monoester content is higher and the technology condition is easier to control. The amphoteric phosphate fatliquor not only has the common characteristics of amphoteric fatliquor, but also can strengthen the characteristics of phosphate esters fatliquor and the cationic fatliquor; therefore it is available used in oil pretreatment before chrome tanning, fractional fatliquor as well as the main fatliquor of high grade leather. Because its molecular structure includes many groups such as amine, phosphate and hydroxyl, the amphoteric phosphate fatliquor becomes the excellent multi-functional active material and is suitable for treating leather fiber in which cationic group such as amine, phosphate and hydroxyl can penetrate into the leather and crosslink with carboxyl and amino groups of leather fiber, thus this kind of reactive fatliquor is also appropriate for fatliquor of metal–free tanned leather. Because amphoteric phosphate fatliquor has many merits, in recent years, it attracts many leather researchers' interest and has become a hot topic in development of new leather fatliquor.

2 Experimental

2.1 Materials and apparatus

Phsophorus pentoxide(AR) was bought from Shanghai Medicine Company. Phosphoric acid (CP) was supplied by Shijiazhuang chemical reagent factory. L-3 fatliquor was industrial reagent and provided by Sichuan TingJiang fine chemical industry. N-Methyl diethanolamine fatty acid esters were self–made. VECTOR 22 IR spectrum machine was supplied by Bruker Company of Germany. TS-2000－S Multi-functional material testing machine was provided by Gaotie Ltd of Taiwan.

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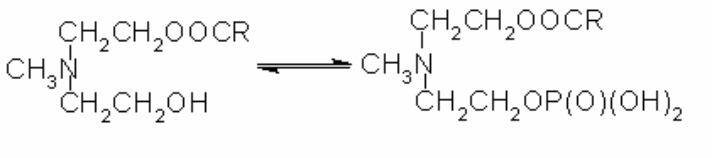
2.2 Synthesis of Polyphosphoric acid

In 250mL four-mouth flask holding mechanical stirrer, thermometer, nitrogen suction pipe, reflux-condenser, isoprestic-ipressure-funnel and gas absorption apparatus, some P_2O_5 powder was added. Then gas tightness of the equipment was examined and the solution was deaerated by bubbling for 15-20min to expel the remaining air and vapor from the equipment. Cold bath was used to control the temperature after the P_2O_5 powder was added, and 85% phosphoric acid in definite proportion was added into flask under 35-40℃. Keeping the temperature and adding the phosphoric acid as quickly as possible, then stirring 42min at constant temperature about 35-40℃. Temperature rise to 100℃ and continuing to react for 30min, then temperature further increased to 200℃ and keeping for 1h, the phosphorylated reagent—polyphosphoric acid was obtained.

2.3 phosphorylating reaction of N-Methyl diethanolamine fatty acid esters

In 250mL three-mouth flask holding thermometer, equipment of temperature control and mechanical stirrer, N-Methyl diethanolamine fatty acid ester was added in definite proportion. When temperature rise to 45℃, 115% polyphosphate was added. Under the reaction temperature and keeping it for some time phosphate ester was obtained. Then temperature was reduced to 50℃, 30% sodium hydroxide was used to neutralize it. After stirring 30min, the emulsifying ability and the pH were examined. The reaction formula was as follows.



2.4 Preparation of Amphoteric Phosphate

Surfactant was essential in fatliquor and it can directly influence the electric properties, emulsifying properties, particle condition and the application performance of fatliquor. Therefore, the research of fatliquor was the development and the application of surfactant. Amphoteric phosphate surfactant which was not mixed with other materials was directly applied on the fatliquor procedure to examine its application performance.

2.5 Determination of Phosphate Ester Content [6-11]

The determination of phosphate ester content was shown in references.

2.6 Determination of zwitterion [12]

According to the reference 12, the zwitterion was determined.

2.7 Determination of Infrared spectrum

Phosphate was washed with saturated salt solution and chloroform in this experiment and dried in oven at 105℃ for 4h, and then it was analyzed with IR apparatus.

2.8 Determination of isoelectric point[13]

Amphoteric surfactant's remarkable characteristic which was different with other surfactants' was isoelectric point that was the common characteristic among the amphoteric compound. When at isoelectric point, solubility of surfactant was the lowest, by which isoelectric point could be determined.

The phosphate potassium sample 1g, was dissolved in the deionized water, then shifted to the 100ml-measuring flask and diluted to the scale division. Some test tubes of dry and diameter similar were taken, adding acetic acid of 0.01mol/L, 0.1mol/L and 1.0mol separately to adjust its pH, measured with pH meter, after shaken up uniformly, lays

aside for10–20min, observing turbid degree in each tube. The pH of solution in which the precipitation was the most was closest to isoelectric point of the amphoteric surfactant.

2.9 Application

The obtained amphoteric phosphate fatliquor was applied in phosphonium tanned leather, compared with the L-3 fatliquor (Sulfited products of mixed vegetable oil).The used chemicals in process all were provided by Cliariant Company.

Process	**%**	**Chemicals**	**°C**	**Min.**	**pH**	**Comments**
Depickling/Taning	80	Water	20			
	7.0	Salt		5		
+		Skins		20	3.4	
+	1.0	Sodium Formate		60	3.5～	
+	2.0	Granofin FCC		120		Over night
+	1.0	Feliderm DP				
	1.0	Catalix U		30		
+	1.5	Sodium Bicarbonate		6×30	5.7	
+	2.0	Tanicor CRF		60		
DRAIN						
WASH	150	Water	20			
+	0.6	Sodium Perborate		60		
DRAIN, WASH, HORSE, Shave to 0.55-0.6mm						
Shaved weight						
WASH	300	Water	40			
	0.5	Tergolix SL-01				
	0.5	Oxalic acid				
	0.2	Feliderm MPP				
	0.1	E.D.T.A.		40	5.6	
WASH						
RETAN	100	Water	35			
	4.0	Granofin TA		60		
	5.0	Tanicor SCU		30		
	1.0	Formic acid		45	3.6	
FATLIQOUR	150	Water	45			
	18	X (fatliquor)		60		
	1.0	Formic acid		10		
	1.0	Formic acid		30	3.3	
Horseing up, over night, drying, staking						

3 Results and Discussion

3.1 Relation between phosphate and time

Firstly the synthesis condition that molar ratio of hydroxyl and the P_2O_5 was n (OH): n (P_2O_5) = 3.0:1.0 and reaction temperature was 75℃ was fixed, a group of exploring experiment was employed to determine reaction time.

The Relation between MAP (monoalkyl phosphoric acid), DAP (diester phosphoric acid), conversion and time along with the time were tested, the results were present in Figure 1 and Figure 2.

Fig. 1 showed that the DAP content was higher at the reaction beginning, but it reduced after 2h, while then the MAP content increased obviously. Because in the reaction process a part of polyphosphate and DAP hydrolyze to MAP, which result in the DAP content reducing and MAP content increasing. The MAP content increased to 80% with 5h; in the later period (5-8h) of reaction, the MAP content didn't change very much along with the time; Figure 2 showed that the curve of relation between conversion and time varied gradually after 5h, which showed reaction achieved the equilibrium after 5h. Therefore according to the above analysis, reaction time was preliminary 6h in this experiment.

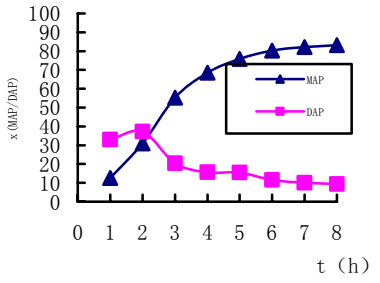


Fig.1 Relation between MAP、DAP and time

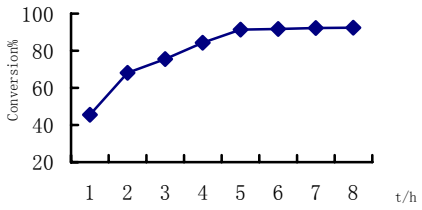


Fig.2 Relation between conversion and time

3.2 Relation between phosphate and material ratio

The condition of reaction temperature 75℃, time 6h was fixed, relation between MAP content and n (OH): n (P_2O_5) was tested; the result was showed in Figure 3.

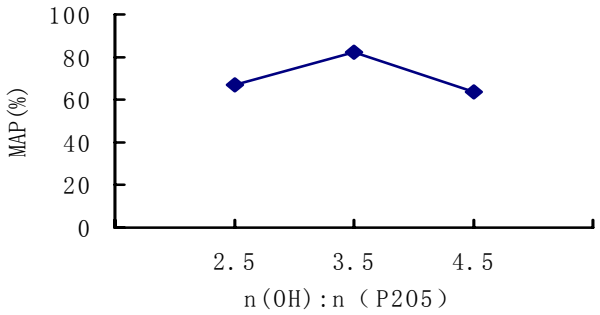


Fig.3 Relation between MAP and n(OH): n（P2O5）

Fig. 3 showed that when n(OH):n(P_2O_5) = 3.5, MAP content was high, when the molar ratio between hydroxyl and P_2O_5 was bigger or smaller than 3.5, MAP content didn't became higher, the preliminary molar ratio in this experiment was that n(OH):n(P_2O_5)=3.5.

3.3 Orthogonal experiment of synthesizing phosphate ester with polyphosphoric acid as phosphorylated reagent

Basing on exploring experiment we optimized the best condition of synthesizing phosphate ester with polyphosphoric acid as phosphorylated reagent. Designing orthogonal experiment and choosing orthogonal table $L_9(3^4)$.

The results of orthogonal test showed that the effect of n(OH):n（P_2O_5）on MAP is the biggest, and the following is

reactive time and reactive temperature. Meantime, we know that the effect of A1 is the biggest in K_A, C_3 is the biggest in K_C. So the optimum condition is $A_1C_3B_2$. From fig.4 we also can see the increasing of n(OH):n（P_2O_5）is not benefit for production of MAP, MAP increases with the increasing of time. When time exceeds by 5.0h, MAP doesn't take on any changing and the color of product will be deeper with time increase. So taking all factors into account, we choose 5.5h as the best reactive time.

Through orthogonal experiment the best condition is that n(OH): n（P_2O_5）is 3.0:1.0, time temperature is 80℃ and reactive time is 5.5h. Under the optimum condition we obtain a production in which MAP is 89.30%, conversion rate of is 97.20%. Repeating the experiment we find reproducibility of the results is good.

3.4 The characterization of amphoteric phosphonate ester surfactant

3.4.1 Identification of amphoteric ions

Bromphenol blue method. Its phenomenon is that the chloroform layer is yellow and the above layer is transparent. Under acid condition amphoteric surfactant possesses cation property. So it can react with bromphenol blue and transfer to chloroform layer, which shows the product has cation property under acid condition.

Methylene blue method. The phenomenon is that chloroform layer takes on blue-purple and the above layer is blue. Under alkaline condition amphoteric surfactant can complex with methylene blue and transfer to chloroform layer, which shows the product has anionic property under alkaline condition.

In a word, the synthesized product is an amphoteric surfactant.

3.4.2 IR analysis

From IR spectrum of N-methyl diethanolamine fatty acid ester and the phosphorylated product we get that the characteristic peak of hydroxyl in 3300 cm-1 exists before phosphorylating reaction and the absorption peak obviously becomes weak after phosphorylating reaction, which indicate that through the phosphorylating reaction, most of hydroxyl in N-methyl diethanolamine fatty acid ester has transformed to phosphate ester. The peak of P=O in (RO)(OH)2P=O exists in 1248 cm-1. The intension of absorption peak between 1170 cm-1 and 1248 cm-1 takes on obvious increasing, which is caused by overlap of the absorption peak of P-O-C and C-O-C. All of these can indicate phosphate ester has been prepared through the reaction which is with polyphosphoric acid as phosphorylated reagent.

3.4.3 The determining results of PI

The pI of the amphoteric surfactant is 3.0-3.5. According to pI amphoteric surfactant can be separated and purified, and its application also can be guided.

3.5 Quality indexes of amphoteric phosphate ester fatliquor

Table 1 The quality indexes of product

appearance	Reddish brown oily liquor
ionicity	amphotericiyt
odor	Sweet and fragrant
emulsification	excellent
Available substances（%）	80%±2%
pH(1:9)	7.5
Stability of latex(1:9)	>24h
Acid-proof, salty-proof and	good

cold-proof stability of latex

3.6 Fatliquoring effects of organic phosphine tanned leather

We oil the organic phosphine tanned leather respectively with prepared amphoteric phosphate ester fatliquor and L-3. The results show that the leather oiled by amphoteric phosphate ester fatliquor is soft, dry and crisp in surface and penetration and combination of fatliquor is good. On the contrast, the leather dealt with L-3 is greasy in surface. The descending of pH after fatliquoring results in fatliquor deposit on surface of leather. Organic phosphine tannage mainly depends on the condensation reaction of hydroxymethyl in tetramethylol and amidogen in leather fiber. There are amidocyanogen, phosphate radical ions and hydroxyl in amphoteric phosphate ester fatliquor, so they can react with carboxyl and amidogen in leather fiber. Because this is the combination between leather fiber and fatliquor, the amphoteric phosphate ester fatliquor can be applicable for oiling of organic phosphine tanned leather.

4 Conclusions

A phosphate ester is synthesized with polyphosphoric acid as phosphorylated reagent. Through orthogonal experiment the best condition is that n(OH): n（P_2O_5）is 3.0：1.0, time temperature is 80℃ and reactive time is 5.5h. Under the optimum condition we obtain a production in which MAP is 89.30%, conversion rate of is 97.20%. The MAP in phosphate ester which synthesized with polyphosphoric acid as phosphorylated reagent and conversion rate are higher than that with P_2O_5 as phosphorylated reagent. In the state the conversion rate is bigger and MAP in synthesized product is more. The most important is that it is more convenient to operate. The results indicate that the leather fatliquored with amphoteric phosphate ester is soft, full and flexible. In its molecules there are amidocyanogen, phosphate radical ions and hydroxyl, which makes it, be efficient and multi-functional active substance. This kind of reactive fatliquor is applicable for oiling of free chrome tanned leather.

Acknowledgments

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