Non-lime-dispersing Agents Acting on Pelt

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Abstract: Taking the time, temperature and dosage as the influencing factors, six non-lime-dispersing agents and lime acted on pelt. As a result of the action, the contents of total protein, proteoglycans and hydroxyproline in treated liquids were measured, and the tissues of chrome tanned leathers were analyzed by scanning electron micrographs and measurement of shrinkage temperature. It is found that one or two parameters are under that of lime when single agent is carried. However, when combining action of two or three agents on pelt, the action effects or three contents measured in treated liquids exceed those of lime. The combination of non-lime-dispersing agent C with D is the best, whose contents of total proteins, proteoglycans and hydroxyproline in liquids are 13.29 mg/mL (10.70 mg/mL in lime), 35.62 μg/mL (31.45 μg/mL in lime) and 72.81 μg/mL (92.49 μg/mL in lime), respectively. Meanwhile, the contents of total proteins, proteoglycans and hydroxyproline in treated liquors are changed with the changes of the treating time, temperature and dosage. Especially, the change of the content of hydroxylproline is more sensitive to the change of temperature.

Key words: pelt; non-lime-dispersing; total protein; polysaccharide; hydroxyproline

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1 Introduction

Liming is a very important process in leather making, whose aim is to make the subsequent tanning agent penetrate into pelt and integrate with collagen efficiently through getting rid of useless substance and loosening collagen fibre. In other words, the purpose of liming is to remove useless interfibre substance and make room for useful materials. After liming process, the appearance of pelt presents as bulk swell and weight increase because of high pH value. A great deal of experiments have indicated that the dispersing extent of collagen fibre does not depend on the swelling degree of pelt, but associates with the removal of interfibre substance and the peptization on collagen of liming agent, which destroys the connection or adhesion in and between collagen molecules.

Lime's low solubility makes the pH value of liming stable, which drives the swelling in a gradual manner and the action on pelt gentle and continuous. At the same time, calcium ion has a special compatibility with collagen, which is favor of removal of interfibre substance. Further more, lime is very

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cheap and practical, so lime is accepted easily by tanneries. However, just because of its characteristic, huge amounts of lime sludge and total solids are formed in liming process, which are the main drawbacks of lime. Thus, lime is one of the main sources of pollution in leather processing.

At present, non-lime swelling system is that non-lime-dispersing agents are employed in high pH value buffer solutions. The fibre bundles of collagen are opened up through the removal of interfibre substance and proteoglycans, which act as inter-fibrillar adhesives of collagen fibrils[1-3]. In this research, several non-lime-dispersing agents are applied in high value buffer solutions, compared with lime. When non-lime-dispersing agents were used alone or in combination, the action effect is assessed through the measurement of total protein, proteoglycans and hydroxyproline contents in treated liquors and the scanning electron microscope (SEM) and the measurement of shrinkage temperature(Ts) of chrome tanned leathers. And the influences on action effect of time, temperature and dosage are studied.

2 Experimental

2.1 Materials

Wet-salted pig hides were chosen as raw material. All the dispersing agents and the chemicals used in experiment were of commercial grade; while the chemicals used for the analysis of leather and treated liquors were of analytical grade.

2.2 Methods and Procedures

The experimental pelts were prepared through soaking and enzyme dehairing processes according to the conventional recipe, and the non-lime swelling process was carried using the following steps (offers were on soaked weight) [4].

Water 80% (desired temperature);

Non-lime-dispersing agent (desired dosage);

Sodium hydroxide until pH 12.5±0.5, run 2 h;

Water 70% (desired temperature), run desired time, drain;

Water 200% (25℃), run 30 min.

In order to have a comparative study, conventional liming process was conducted as the follows. The pelt sample was treated with 80% water (25℃), 1% sodium sulfide and 6.0% lime. Two hours later, 70% water (25℃) was added, and the drum was run for 36 h. Then the liming liquor was drained, and the limed sample was washed with 200% water (25℃) for 30 min.

After swelling or liming process, the swelled or limed weight of pelts was noted. The dosages of chemicals in the latter processes were based on this weight. Then the pelts from swelling and liming processes were converted into chrome tanned leathers using conventional deliming, bating, pickling and tanning recipes together.

In the first part of experiment, non-lime-dispersing agent was used alone, and the desired temperature, dosage and time were 25℃, 1.5% and 36 h, respectively. The treated liquor was collected, which included processed water and washed water. The total protein, proteoglycans and hydroxyproline contents in treated liquors were analyzed as per the standard procedures[5-8]. A scanning electron microscope was used for analysis of the opening up extent of fibre bundles, and the shrinkage temperature of chrome tanned samples was tested.

After the first part of experiment, three non-lime-dispersing agents with good dispersing ability of fibre bundles were determined. Then the two or three non-lime-dispersing agents were combined with equal ratio, and were applied in swelling process, and the desired temperature, dosage and time were also 25℃, 1.5% and 36 h, respectively. The cooperative effect was analyzed through the measurement of the contents of total protein, proteoglycans and hydroxyproline in treated liquors.

In the part of examination of influence of time on action effect, the desired temperature and dosage were 25℃ and 1.5%, respectively. The time was set to 14 h, 18 h, 24 h, 36 h and 48h. When the influence of temperature on action effect was examined, the desired time and dosage were 36 h and 1.5%, respectively. The temperature was set to 18℃, 20℃, 25℃, 28℃ and 32℃.When the influence of dosage on dispersing ability was examined, the desired temperature and time were 25℃ and 36 h, respectively. The dosage was set to 1.0%, 1.5%, 2.0%, 2.5%, 3.0% and 5.0%.

3 Results and discussion

3.1 Action Effect of Non-Liming Agent

The contents of total proteins, proteoglycans and hydroxyproline in treated liquors indicate the action effect of non-liming agent. The content of total proteins shows the removal extent of non-collagenous proteins, and the removal of proteoglycans contributes a lot to the opening up of fibre bundles, which act as inter-fibrillar adhesives of collagen fibrils. The content of hydroxyproline shows the hydrolytic extent of collagen during process. The contents of total proteins, proteoglycans and hydroxyproline in treated liquors are given in Tab. 1. The contents of total proteins of non-lime-dispersing agent C and E are higher than that of lime, and the content of non-lime-dispersing agent D is almost same as lime. The proteoglycans contents of non-lime-dispersing agent A, C and D are comparable to that of lime, and the proteoglycans contents in non-lime-dispersing agent E and F are a little lower than lime. From the two aspects, it is concluded that non-lime-dispersing agent C, D and E could removal more non-collagenous materials, which means the three non-lime-dispersing agents split fibre bundles better than the others. Apparently, except for non-lime-dispersing agent E, the contents of hydroxyproline of the other non-lime-dispersing agents are higher than that of lime, which shows non-lime-dispersing agents can protect collage well.

The shrinkage temperatures of chrome tanned leathers are shown in Tab. 1. The shrinkage temperatures of chrome tanned leathers processed by non-lime-dispersing agent C, D and E are higher than the other dispersing agents and lime. High shrinkage temperature indicates good opening up of fibre bundles. So non-lime-dispersing agent C, D and E loose collagen fibre better than the others, which is coincident with the analysis of contents of total proteins, proteoglycans and hydroxyproline in treated liquors.

Tab. 1 Contents of total proteins, proteoglycans and hydroxyproline in treated liquors and Ts of chrome tanned leathers

Item	A	B	C	D	E	F	Lime
Total protein/(mg/mL)	5.65	5.79	16.84	10.62	13.25	6.41	10.70
Proteoglycans /(μg/mL)	32.96	17.76	32.83	39.52	26.32	26.34	31.45
Hydroxyproline /(μg/mL)	78.59	60.12	83.31	67.78	92.56	71.84	92.49
Ts/℃	93.9	93.5	95.8	95.0	95.9	93.6	92.3

The scanning electron micrographs of chrome tanned leathers showing the cross-section are given in Fig. 1. The scanning electron micrographs of non-lime-dispersing agent C, D and E show fine fibre bundles compared to the other chrome tanned leathers. This indicates that non-lime-dispersing agent C, D and E disperse collagen fibre better than the others, which is coincident with the analysis of contents of total proteins, proteoglycans and hydroxyproline in treated liquors and the shrinkage temperature of chrome tanned leathers. So the three non-lime-dispersing agents are choosen as materials for the study on combining action effect of non-lime-dispersing agent.

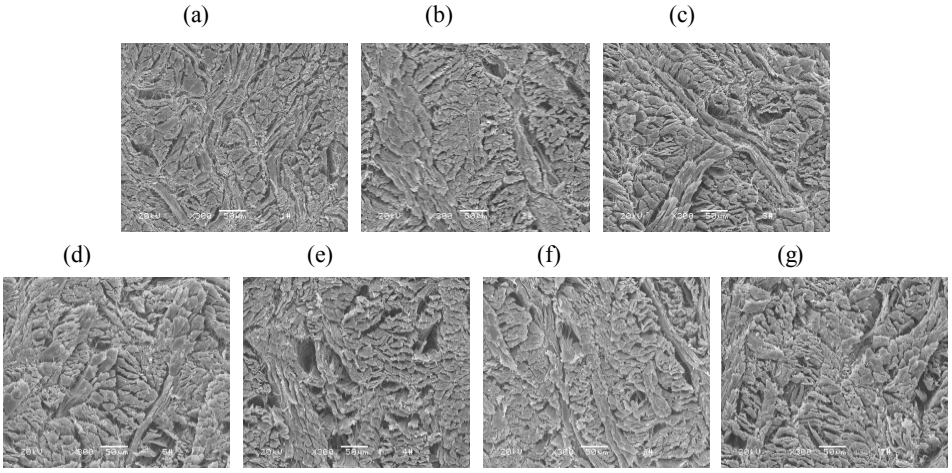

Fig. 1 Scanning electron micrographs of chrome tanned leathers showing cross section (×300); (a)~(f): corresponding to chrome tanning leathers processed by non-lime-dispersing agent A~F, respectively; g): chrome tanned leather processed by lime.

3.2 Combining Action Effect of Non-Lime-Dispersing Agents

The contents of total proteins, proteoglycans and hydroxyproline in treated liquors processed by

combinations of two or three of non-liming agent C, D and E are given in Tab. 2. The content of total proteins in combination of non-lime-dispersing agent C and D treated water is lower than that of non-lime-dispersing agent C and higher than that of non-lime-dispersing agent D. The contents of proteoglycans and hydroxyproline in treated liquors are also between those of non-lime-dispersing agent C and D. The other combinations of non-liming agent C and E, D and E, and C, D and E have same results as the combination of non-liming agent C and D. That is to say the action effect of each non-lime-dispersing agent can be integrated when they are combined. It is also concluded that the combination of non-lime-dispersing agent C and D is the best, which removes inter-fibrillar substance more effectually than lime and protects collagen better than lime. So it was choose to be the non-lime swelling agent when the influences on action effect of time, temperature and dosage were studied.

Tab. 2 Contents of total proteins, proteoglycans and hydroxyproline in compositely processed water

item	C and D	C and E	D and E	C, D and E	lime
Total proteins/(mg/mL)	13.29	16.67	11.24	13.68	10.70
Proteoglycans /(μg/mL)	35.62	28.21	33.56	27.59	31.45
Hydroxyproline /(μg/mL)	72.81	83.89	75.68	86.87	92.49

3.3 Influence on Action Efffect of Time, Temperature and Dosage

The curves of the contents of total proteins, proteoglycans and hydroxyproline in treated liquors against time, temperature and dosage are given in Fig.2, Fig 3 and Fig 4, repectively. It can be seen that the contents of total proteins, proteoglycans and hydroxyproline in treated liquors are improved with the prolonging of time, the elevation of temperature and the increase of dosage, which means that the extent of opening up of fibre bundles and the hydrolytic extent of collagen are enhanced with the prolonging of time, the elevation of temperature and the increase of dosage. It also can be included that the increases of the contents of total proteins, proteoglycans in treated liquors is slow when the treating time is over 24 h, the temperature is above 25 ℃ and the dosage excesses 20%, but the increase of the content of hydroxyproline in treated liquors is violent. Especially, the change of the content of hydroxylproline is more sensitive to the improvement of temperature. In another word, the collagen would be overly hydrolyzed if the treating temperature is too high. In a word, the optimal treating time, temperature and dosage for non-lime-dispersing agent are 24 h, 25℃ and 1.5%. But if one of the three factors is not at the optimal treating condition, it can be balanced by adjusting the other two factors to get good dispersing effect. For example, if the temperature is low in winter, the prolonging time and increasing dosage can be adopted for enough extent of opening up of fibre bundles.

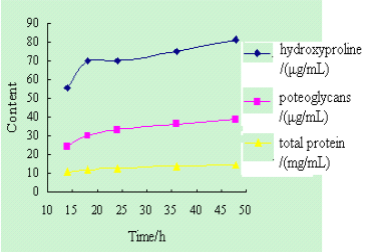

Fig. 2 Time *vs* contents of Total proteins, proteoglycans and hydroxyproline

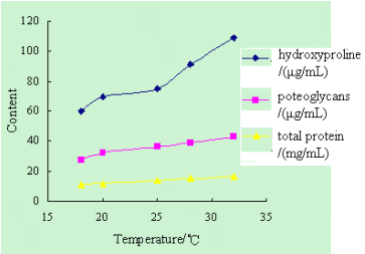

Fig. 3 Temperature *vs* contents of total proteins, proteoglycans and hydroxyproline

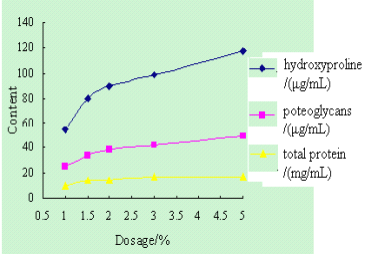

Fig. 4 Dosage *vs* contents of total proteins, proteoglycans and hydroxyproline

4 Conclusions

(1) In spite of one or two parameters are under those of lime, non-lime-dispersing agent C, D and E split fibre bundles better than the other non-lime-dispersing agents.

(2) The combined application of two or three non-lime-dispersing agents can integrate the action effect of each non-lime-dispersing agent, and the combination of non-lime-dispersing agent C and D is the best, whose contents of total proteins, proteoglycans and hydroxyproline in liquids are 13.29 mg/mL (10.70 mg/mL in lime), 35.62 μg/mL (31.45 μg/mL in lime) and 72.81 μg/mL (92.49 μg/mL in lime), respectively.

(3) The extent of opening up of fibre bundles and the hydrolytic extent of collagen are enhanced with the prolonging of time, the elevation of temperature and the increase of dosage, and the change of hydrolytic extent of collagen is more violent than the change of extent of opening up of fibre bundles. Especially, the change of the content of hydroxylproline is more sensitive to the change of temperature.

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