DEVELOPMENT AND PRACTICAL APPLICATION OF UNHAIRING METHOD WITHOUT USING SULFIDE

K. Takase [1], M. Terashima [1] and K. Yoshimura [2]

1 Tokyo Metropolitan Leather Technology Center, 3-3-14, Higashisumida, Sumida-ku, Tokyo, 131-0042, Japan, +81-3-3616-1671,a) takase.kazuya@hikaku.metro.tokyo.jp b) terashima.mariko@hikaku.metro.tokyo.jp

2 Japan Leather and Leather Goods Industries Association, 1-12-13, Komagata, Taito-ku, Tokyo, 111-0043, Japan, +81-3-3847-1451, yoshimurak@leather.onmicrosoft.com

Abstract. Leather manufacturing industry uses a lot of water and chemicals, and it discharges large amounts of wastewater. The processing a large amounts of wastewater requires a huge cost. Therefore, reduction of amount of a pollution load in wastewater is a theme in many countries around the world. During the leather process, a lot of pollutants occur in the unhairing process. Some estimate that the amount of pollution generated in the unhairing process accounts for 70% of the entire leather manufacturing process. In this unhairing process, usually a large amount of sulfide is used. Sulfide is known to generate hydrogen sulfide and cause damage to the drain pipe. In Tokyo, strict criteria are set for draining sulfide to sewers. Therefore, reducing the amount of sulfide used is an important task for tanner. In addition, since sulfide has no degreasing effect, a large amount of surfactant is required in the unhairing process. However, to reduce the cost and the load of the wastewater, it is also required to reduce the amount of the surfactant used. Therefore, development of a method of effectively removing hair loss and degreasing without using a sulfide is urgent for the leather manufacturing industry. On the other hand, pelts are widely used as raw materials for foods such as gelatin and collagen casing, cosmetics, and pharmaceuticals. However, sulfides are not recognized as food additives in Japan. Sulfides are not recognized as food additives in Japan. Therefore, some companies are concerned about using pelts as a raw material for food using sulfide in the unhairing process. Also from this point of view, it is necessary to develop an unhairing method without using sulfides. The method using sodium hydroxide has been studied for a long time. However, this method is hard in handling, and is difficult to set conditions such as concentration and temperature. That is, while successful at the experimental level, it has not been put to practical use. Therefore, we studied a method to solve the above problem using sodium hydroxide. The method developed this time can reduce the pollutant in waste water, and the amount of water used in the unhairing process to 1/10 or less of the conventional one. Moreover, since it is not influenced by water temperature, it made it possible to stably remove hair irrespective of the season. The finished leather kept sufficient strength. In addition, sodium hydroxide reacts with fat in the skin and turns it into soap, so it shows the degreasing effect and contributes to reduce the dosage of degreasing agent.

1 Introduction

At present, production with reduced environment load is one of the most important issues for the manufacturing industry. In reducing environment load, there are various issues such as resource saving, effective use of waste, and the use of safe substances in the manufacturing process. Emphasis on reducing environment load affects the evaluation criteria of companies and may change consumers' buying behavior.

Also for tanners, it is required to make products with reduced environment load. The environment-friendly issues in the leather manufacturing industry include various things such as resource saving, water saving, reduction of wastewater pollution load, efficient wastewater treatment, and effective use of waste. In particular, in order to continue making leather stably even in developing countries where wastewater treatment facilities are not sufficiently developed, establishing a recipe that contains less waste and is easy to treat wastewater is an extremely important issue .

However, these problems span each process, and it is extremely difficult to solve them at one time. Also, among these tasks, there are many that are difficult to cope with immediately. For

example, when there is no substitute, or when there is a cost increase. Nevertheless, environmental-friendly corporate activities are a global trend, and the formulation of measures is urgently needed.

In this study, we focused on the unhairing process, which is considered to have the highest wastewater pollution load among the leather making processes, and examined methods to minimize the load in this process.

In the unhairing process, it is said that it accounts for 70% of the wastewater pollution drained in the leather making process. By reducing the wastewater pollution in this process, the reduction effect of the whole process can be expected. The treatment of the wastewater generated in the unhairing process is one of the difficult problems. The cause of the high wastewater pollution load in the unhairing process includes the use of sodium sulfide and sodium hydrosulfide. Sodium sulfide has long been used in the unhairing process. It is considered that the cost of medicine is lower than other methods, and it is easy and effective. However, iodine consumption is greatly increased by using sodium sulfide. When a sulfide is used, it is about 20,000 mg/L. On the other hand, in Japan's sewers, drainage standards are set at less than 220 mg / L. The reference value of the iodine consumption is determined because, if the value is high, hydrogen sulfide generated from the waste water is oxidized to change to sulfuric acid. The generated sulfuric acid corrodes due to chemical reaction such as metal and concrete, which causes a big problem in maintaining and managing the sewerage. If the corrosion and deterioration of the pipeline facilities proceed, not only the maintenance cost will increase but also the loss of the pipe will cause the depression of the road and the contamination of ground water. In order to reduce iodine consumption, it is known that the oxidation method by aeration processing is effective. However, aeration of wastewater with high iodine consumption may generate toxic gas such as hydrogen sulfide. Therefore, it may cause problems at the sewage treatment plant. Sodium sulfide is disliked also from this point.

It is conceivable that the most reliable way of suppressing the generation of hydrogen sulfide is not to use sodium sulfide. A variety of enzymatic unhairing methods have been investigated as an alternative method that does not use sulfides. Since enzyme unhairing generally does not dissolve hair, reduction of COD and BOD other than iodine consumption can be expected. However, the fallen hairs need to be recovered and become an obstacle in the operation. In addition, since the hair is removed by loosening the hair roots, no effect can be expected on skins without reticular layers such as pigs.

On the other hand, the hair removal method by sodium hydroxide has been studied for a long time. Although, the formulation used in the past is not practical because the amount of water used is so large as 300%, and the drum is loaded. Also, according to our previous experiments, it was extremely difficult to produce stable quality products throughout the seasons, as it is influenced by water temperature when there is much quantity of water. Therefore, in the present study, we investigated the unhairing method for pig skins, using sodium hydroxide and potassium hydroxide with small amount of water.

We applied this method and tried to remove hair and make leather on a pilot scale.

2 Materials and Methods

2.1 Materials

Pig skins were purchased from raw material traders in Tokyo. Sodium hydroxide was used as a commercially available 48% solution (w / w), and potassium hydroxide was used as a 50% solution (w / w) in granular form. For unhairing, these solutions were used undiluted or diluted with a small amount of water.

2.2 Unhairing and tanning prescription

The methods from unhairing to tanning are shown in Table 1. 6.5 to 20% of sodium hydroxide was added per weight of raw hide. The amount added was determined based on the season and temperature. At this time, the molecular weight of potassium hydroxide was about 1.4 times that of sodium hydroxide, so the amount added was also 1.4 times that of sodium hydroxide. In addition, sodium chloride was added for sodium hydroxide and potassium chloride was added for potassium hydroxide in the reaction step in order to suppress skin swelling. Furthermore, in order to establish unhairing conditions, the relationship between the concentration of the aqueous solution and the reaction temperature was examined.

Table 1. Unhairing with sodium hydroxide and tanning process.

Process	Dosage(%)	Chemicals	Temperature(℃)	Time (minutes)
Flush		Water		10
Unhairing	7.5	Sodium hydroxide.aq(48%)	28	40
	10	Sodium chloride	28	60
Flush				5
Liming	250	Water	25	
	3.0	Slaked lime		
	0.4	Surfactant		180
Stirring				30
Flush				5
Deliming	100	Water	32	
	3.0	Ammonium chloride		
	0.4	Surfactant		30
Flush				5
Pickling	10	Water	25	
	6.0	Sodium chloride		10
	0.4	Surfactant		
	6.0	Formic acid		
		1/3		10
		1/3		10
		1/3		60
Tanning	8.0	Chrome tanning agent	30	
	1.6	Sodium hydrogen carbonate		
		1/3		10
		1/3		10
		1/3		20
	0.1	Antifungal agent		
Stirring				30
pH adjustment	1.0	Sodium hydrogen carbonate	25	20
Horse up				

2.3 Physical property measurement

Tensile strength, elongation and tear strength of the leathers made from the above-mentioned recipe were measured based on JIS K 6550 (Japanese Industrial Standards). Six pig leathers were prepared for the test. For each leather, six test samples were cut out for each test from the site defined by JIS K 6550. That is, the test sample was 6 sheets × 6 points / sheet = 36 points. The same test was also performed on leathers made of depilated skin using sodium sulfide and sodium hydrosulfide.

3 Results and Discussion

3.1 Results of unhairing

Unhairing was completed approximately 40 minutes after adding sodium hydroxide. Figure 1 shows the appearance of pelt after unhairing has been completed. Pelts depilated with sodium hydroxide had a higher degree of whiteness compared to the one using sulfide (Figure 2). This may be due to the low sulfur content. This feature is considered to be advantageous for making white or light colored leather.

Fig. 1. The appearance of pelt after unhairing

Fig. 2. Pelts depilated with sodium hydroxide

3.2 Relationship between sodium hydroxide concentration and reaction temperature

The relationship between the sodium hydroxide concentration and the reaction temperature was examined based on the successful depilatory recipe. As a result, it was shown that the relationship is almost linear (Figure 3). It is thought that unhairing will be successful near the straight line.

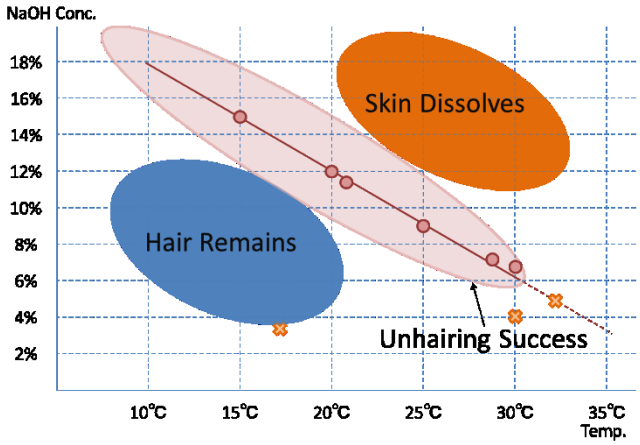

Fig. 3. Relationship between the sodium hydroxide concentration and temperature

3.3 Physical property (tensile strength, elongation, tear strength)

The results of physical property measurement are shown in Table 2. The numbers in parentheses indicate the standard deviation.

The difference between the two was tested by t-test. The tensile strength was not significantly different at a t value of 0.07274>0.05. As for the elongation, there was a significant difference between the two at a t value of 2.4332×10^{-17} <0.05. Tear strength was significantly different between the two at a t value of 2.1342×10^{-8} <0.05. That is, there was no significant difference in tensile strength between the two. On the other hand, regarding the elongation and tear strength, the leather made of sodium hydroxide was shown to be easy to stretch and flexible, and to be superior in tear strength.

Table 2. Effect of the chemicals for unhairing on physical properties

Chemicals for unhairing / Test item (unit)	Sodium Hydroxide	Sodium Sulfide
Number of sample	36	36
Tensile Strength (MPa)	10.6(2.1)	11.7(3.1)
Elongation (%)	54.2(10.8)	36.2(7.8)
Tear strength (N/mm)	24.1(2.8)	19.2(3.6)

4 Conclusion

We have developed a different method of unhairing. That is, a method using sodium hydroxide with small amount of water for pig skins. The features of the method developed this time are water saving, shortening of the unhairing process, simplification of wastewater treatment and reduction of degreasing agent usage. Methods developed in the past used a large amount of water, with a float of 300%. Therefore, it was extremely difficult to control the temperature, and it was hard to stably remove hair using only sodium hydroxide.

As mentioned above, in this formulation, when the water temperature exceeded 20 °C., the pelts tended to become weak. Moreover, when the ratio of the float was large, the skin swelled in alkali, and it was not avoided that the grain of the skin was damaged. These problems could be achieved by using a high concentration sodium hydroxide solution and reducing the amount of float. At this

time, since a commercially available liquid medicine was used as a stock solution or diluted with a small amount of water, the float was about 30%, and it was possible to significantly reduce the amount of water used. Also, the time required for unhairing could be significantly reduced compared to sodium sulfide.

The sodium hydroxide used in the unhairing process reacts with the fat in the skin and turns into a soap, so that a degreasing effect was also exhibited. In particular, pig skin is more fat than other animal species.

Therefore, a large amount of surfactant is required for degreasing, which causes an increase in manufacturing cost. Since it is possible with inexpensive sodium hydroxide, cost reduction can also be expected.

In the prescription used this time, the bating process using an enzyme was omitted. In general, it is considered that, by performing bating, it is possible to make the leather flexible, stretchable, and smooth grain. Although the smoothness of the grain was not examined, the elongation showed a high value as compared with that of the depilated by sodium sulfide. That is, it has been suggested that a leather with high elongation can be produced without the bating process. Also in this respect, it has been shown that the use of sodium hydroxide can contribute to simplification of the working process. By applying this method, it may be possible to make leather in a way with less environmental load than the recipe we implemented this time.

From now on, by examining the effective utilization of wastewater, we would like to realize saving of water in the leather making process and reduction of wastewater treatment cost.

It is also possible to make gelatin and collagen peptide from pelts that has been depilated by this formulation, and it can be expected to make food safer than before. We plan to develop this matter as well.