

## BUFFER ACTION OF SAPONINS

### Part II.—Their Use as Depickling Agent

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Saponin solutions have been evaluated for their depickling properties. These are attributed to their buffer activity, surface activity and to a slight amount of pretannage.

It has been pointed out earlier that the saponins are useful buffers in the 3.5 to 5.0 pH range.<sup>1</sup> Since depickling of the pelt also takes place in the same pH range, we have investigated the use of saponins for this purpose. Depickling depends on the ease of removal of the pickling acid, hence substances which can diffuse out the latter from the pelt before neutralisation, are useful. Because of their surface activity saponins might prove effective on these lines.

### Experimental

Goatskins and sheepskins were subjected to the standard processes of soaking, unhairing, liming, deliming and bating. The test pieces were pickled with different concentrations of sulphuric acid so that pickled pieces having an acidity of 1.1 to 2.5 pH units were obtained. The pelts were then divided into six lots for comparative study with different depickling agents, viz. sodium carbonate, sodium bicarbonate, sodium thiosulphate, borax, saponin and mixtures of saponin and sodium acetate.

Depickling was effected with 2% solution of the various reagents. 4×6 in pieces of goatskin were introduced into a 200–400% float with 2–10% salt. All percentages were based on pelt weight. The chemicals were added in small portions and the pieces were shaken for 15–30 min each time. The pH was checked by means of the universal indicator paper and by using a Cambridge pH meter.

Tables 1–4 list the variance of the pH of the liquor having different original acidity on the gradual addition of saponins and the other depickling agents and also record subsequent observation regarding the quality of finished leather.

### Discussion

Pickled pelts are known to contain a small percentage of acid and salt. These must be removed in order to prepare the pelt for tannage. One way of doing this would be to immerse the pelt in water. But this would lower the salt content and would swell the pelt. Addition of more salt may prevent this swelling but would not remove the acid. One of the methods adopted in the leather industry is depickling which is neutralization of the acid by means of alkalis or buffers. The use of alkali solutions is, however, discouraged. Our own experiments with alkaline solutions reveal that the resulting leather does not have the desired feel. This is not unexpected since pickled pelts are in a state in which a large number of cross-linkages have been cleaved and a quick removal of the acid and salt would not produce the desired conditions in which the pelt should be prior to tannage. It is for this reason that depickling agents which are buffers in the pH range of 2.5–4.0 are used. These are considered safe since the leather obtained from these treatments have a soft feel.

Depickling then prepares the pelt for tannage. The pH is required to be adjusted to the desired acidity so that the proper groups are available for coordination.<sup>2</sup> The usual pH attained through depickling is 2.5–5.0 which is sufficient to bring the pelt in the tanning range.<sup>3</sup> The two accepted depickling agents are borax and sodium thiosulphate. The solutions of saponin have a pH range of 3.5–5.0 depending upon dilution. Since the maintenance of acidity is desirable, and since no ill effects are observed, this buffer system may also be classified as a safe depickling agent.

The depickling reaction of the saponins is possibly a combination of three properties: (i) their buffer action, (ii) slight amount of pretannage and (iii) their surface activity.

TABLE 1.—DEPICKLING OF PELTS AT pH 2.5 WITH DIFFERENT DEPICKLING AGENTS.

	Borax	Sodium acetate	Sodium carbonate	Sodium bicarbonate	Sodium thiosulphate	Saponin
Original pH of 2% test solution	9.1	7.9	10.9	8.3	7.6	4.3
pH of 400% float 5% salt after addition of 2% test solution and drumming for 5 min	8.6	5.8	10.6	9.6	5.6	5.2
pH after drumming for 30 min with the pelt	5.5	5.4	7.8	6.8	3.9	4.4
<i>Observation after depickling</i>	silky feel, smooth grain, not plumped	no silky feel, smooth grain, not plumped	slippery feel, grain pronounced, not plumped	slippery feel, grain less pronounced, not plumped	silky feel, smooth grain, not plumped	smooth feel, grain smooth, not so plumped, colour of pelt not as white as in hypo

TABLE 2.—DEPICKLING OF PELT AT pH 1.5 WITH DIFFERENT DEPICKLING AGENTS.

	Borax	Sodium acetate	Sodium carbonate	Sodium bicarbonate	Sodium thiosulphate	Saponin
Original pH of 2% test solution	9.1	7.9	10.9	8.3	7.6	4.3
pH of 200% float 2% salt after addition of 2% test solution and drumming for 5 min	2.5	2.7	4.0	3.2	3.9	3.5
pH after drumming for 30 min	2.9	3.4	3.4	3.3	3.4	2.8
<i>Observation after depickling</i>	rubbery feel, smooth grain, quite plumped	no silky feel, grain smooth, very plumped	very harsh feel, grain pronounced, plumped	harsh feel, grain not so smooth, slightly plumped	less silky feel, grain smooth, not plumped	rubbery feel, grain smooth, little plumped

TABLE 3.—DEPICKLING OF PELT AT pH 1.1 USING SAPONIN, SODIUM THIOSULPHATE AND BORAX.

	Saponin	Sodium thiosulphate	Borax
Original pH of 2% test solution	4.3	7.6	9.1
pH of 200% float and 10% salt after drumming with pelts for 10 min	1.65	1.6	1.55
pH after addition of the test solution 0.5%	1.45	1.5	1.5
pH after addition of 25% float and drumming for 15 min			
pH after addition of 0.5% solution	1.95	1.95	2.0
pH after addition of 25% float and 15 min drumming	2.1		
pH after addition of another 0.5% test so solution and drumming for 15 min		2.4	2.9
Shrinkage test	39°C	38°C	38°C
<i>Observation after depickling</i>	bit soft and silky feel, smooth grain, very slight plumpness	bit harsh feel, smooth grain, no plumpness	silky feel, grain not as harsh, slight plumpness

TABLE 4.—DEPICKLING OF pH 1.15 USING MIXTURES OF SAPONIN AND SODIUM ACETATE AS DEPICKLING AGENTS.

	Saponin 25% sodium acetate 75%	Saponin 50% sodium acetate 50%	Saponin 75% sodium acetate 25%
Original pH of 2% test solution	6.15	5.05	4.9
pH of 200% float and 10% salt after addition of 1% test solution and drumming for 1 hr	2.65	1.75	1.7
pH after addition of another 1% mixture and drumming for 45 min	3.55	2.25	2.25
Observation after depickling	very soft feel, pronounced grain, slightly plumped	soft feel, pronounced grain, slightly plumped	soft feel, more pronounced, slight plumpness

In the case of vegetable tannages, it is not necessary to depickle the pelt since it has been found that these materials contain weak acids.<sup>4</sup> This action has been shown to be due to the property of such acids or their salts to remove the mineral acid from the pelt. Saponins being weak acids fall under this category and hence a small amount of this material may be useful in the mineral and vegetable tannage processes particularly because there is no risk of an increase of pH to a high level as in the case of borax or other bases.

It was mentioned in the earlier communication that the addition of sodium acetate enhances the buffer activity of the saponin. This mixture also works better as a depickling agent since a good quality leather is obtained in this manner as is evidenced by Table 4.

In the case of pelts which were pickled below pH 1.0 gelatinization had already occurred and none of the depickling agents was of any help. Consequently the leather obtained in each case was of a papery feel which could not stand the  $T_s$  tests. Some difficulty was experienced in obtaining the desired pH when pelts pickled at pH 1.0 to 1.5 were tried with the usual reagents. The results shown in Table 3 bear out this point. The leather obtained from pelts pickled at pH 1.5 to 3.0 were, however, depickled as easily by saponins as by sodium thiosulphate solution. This action may be assigned to the similarity in the properties of the two reagents towards collagen.

*Pretannage.*—Saponins do not seem to have any tanning properties since they do not produce an

immediate turbidity in a solution of gelatin. On standing, however, a slight turbidity is noticeable. This might be due to a very slight tanning reaction, if at all. As indicated above the depickling reaction with saponins is comparable with sodium thiosulphate. Since the latter is known to produce sulphur pretannage,<sup>5</sup> a similar reaction with the former is indicated. It is quite likely that the hydroxyl group of the saponins leads to this type of tannage as for vegetable tannins.

*Surface Activity.*—This property might be responsible for the ease in the removal of the acid and its salt from the pelt. The surface activity of the saponins is well established. Their molecules possibly penetrate the pelt and remove the adhering salts or other molecules along with their solutions. This is indicated by the rise in pH on the addition of float and a slight but significant decrease in pH on the addition of saponin. This may be due to the washing out of the acid and salt on the addition of the saponin solution.

#### References

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