

Borates in leather manufacturing

1. Introduction

Both Borax Decahydrate and *Optibor*[®] boric acid came into use in the leather industry in the latter half of the 19th century. It is the mild alkalinity of borax and weak acidity of boric acid that make them suitable for this application. Borax is used for soaking hides and skins, for stripping vegetable tans and for neutralizing chrome tans. Boric acid is used mainly for neutralizing limed pelts.

2. Curing hides and skins

Hides and skins are usually cured by drying or salting to preserve them during storage or transportation before they are tanned. Many other preservatives are commercially available to help prevent attack from fungi, mold and bacteria.

3. Soaking

At a tannery, the first process applied to hides and skins is a water soak used to clean and remove any salt. Borax added to the soak imparts slight alkalinity and provides a safe and effective soaking agent for many types of goods including woolled skins. It is used in concentrations of 0.5-1.5 kg per 1,000 liters (5-15 lb. per 1000 gallons). Soaking time and temperature required depend on the nature of the hides and the type of leather to be produced.

4. Neutralizing (deliming)

After soaking, a liming process is used to loosen hair on the hides or skins in preparation for tanning. The hides are soaked in a solution of Calcium hydroxide (lime) which leaves the pelts very alkaline (a pH of about 12.5). Based on the type of leather being made, part or all of the lime has to be neutralized prior to tanning. For sole leather, which is required to be firm and hard, it is usual to neutralize the grain layer only, while for more flexible leathers, such as shoe uppers, complete neutralization is common. Neutralization is achieved by washing with water, followed by treatment with a solution containing an acid, an acid salt such as sodium bisulfite, or the salt of a weak base, such as ammonia.

The pH values of the acids most widely used for neutralization areas follows:

Acid	Concentration (kg/1000 liter)	pH of Solution
Hydrochloric	13.2	1.1
Lactic	9.0	2.4
Acetic	6.0	2.9
Boric acid	6.2	5.6

Hydrochloric acid, although a cheap acid, is also the strongest and is liable to cause plumping of the outer layers of the pelt which prevents penetration of the acid to its interior. "Case Hardening" can occur and lead to a coarser grain. Boric acid, the weakest of the acids listed, will not cause swelling of the pelt, and leads to leather with a smooth, good-colored, non-cracky grain.

Neutralization follows the following reaction: $\text{CaO} + 3\text{H}_3\text{BO}_3 \implies \text{Ca}(\text{BO}_2)_2 + 3\text{H}_2\text{O}$

It can be calculated that 1 part of lime (CaO) needs 2.2 parts of boric acid. The lime content of pelt varies from about 0.5-2.0%. Pelts containing 1% lime would theoretically need 2.2% *Optibor*® boric acid by weight of the pelt for complete neutralization. In practice it is found that more than this is required. For many purposes, e.g. vegetable sole and belting leathers, it is unnecessary to neutralize completely and 2-2.5% boric acid is sufficient.

One can economize on the cost of using boric acid while still obtaining its advantages by employing it in association with a cheaper mineral acid in one of the following ways:

4.1 Regeneration and restrengthening method

After removing the pelt, the volume of the neutralization bath is restored to its original level. Dilute sulfuric acid is added to render the bath mildly acidic (pH of 4.0-5.0), converting the calcium borate to its equivalent of free boric acid. The bath is left to allow calcium sulfate to crystallize out and settle. Boric acid is then added to replace the amount neutralized by the pelt. This process can be carried out for a number of times until the bath is too contaminated by dissolved protein matter from the pelt.

4.2 Periodic regeneration during neutralizing

In this method a smaller amount of boric acid may be used to start with, e.g. 1.5%. At intervals during the neutralizing process, suitable amounts of mineral acid, such as hydrochloric acid, may be added to bring the pH back to 4.0-5.0, converting the calcium borate that is present. Alternatively, Borax Decahydrate and hydrochloric acid may be added to generate the boric acid. Once the pelt is introduced, a suitable amount of acid is added at intervals to render the bath mildly acidic. Removal of the pelt will remove some boric acid from the bath. The used bath can be restrengthened with Borax and regenerated with hydrochloric acid. However, this cannot be repeated too many times because of the accumulation of calcium chloride in the bath. This type of process is particularly suitable for drum neutralizing.

4.3 Use of a *Optibor*® (boric acid)-hydrochloric acid mixture

This process uses a mixture of boric acid and hydrochloric acid. The strong acid is rapidly used up by the lime in the outer layers, leaving the final neutralizing to be achieved by *Optibor*® boric acid.

In the above mentioned methods, the degree of neutralizing is measured by means of a phenolphthalein indicator. The pelt is cut at the thickest part and an indicator solution is applied to the cut surface. The neutralized zone remains colorless, while the limed zone turns pink.

It is important to use sufficient boric acid for complete neutralization. If the pelt is left in such a bath too long, e.g. overnight, the lime diffuses out from the center, rendering the outer zones once more alkaline. After neutralizing, it is desirable to rinse the pelt to remove the slightly soluble calcium borate.

5. Stripping vegetable-tanned leathers

One of the more important uses of Borax Decahydrate is for stripping vegetable-tanned crust (tanned and dried) leathers, either as a stage in the dressing to finished and dyed vegetable leathers or as a preparation for re-tanning them with another agent. Borax Decahydrate, sodium bicarbonate and sodium carbonate are commonly used for the stripping process to remove some of the tannin in the leather, especially from the surface layers. Borax Decahydrate provides solutions of suitable alkalinity for this process, when compared to sodium carbonate which may be too alkaline lead to over-stripping.

In carrying out the stripping process, the crust leather is soaked, sammed and shaved if necessary. It is then placed in a water float at 35°C and a solution of a suitable amount of a stripping agent is slowly run through. Care must be taken to avoid contact of the stripping agent with the leather. After about 30 minutes the liquor is drained and the leather is washed. This is essential to remove solubilized tannin and salts which might later cause discoloration. The leather may then be 'cleared' by drumming in a weak solution of sulfuric acid, after which it is again washed. The amount of stripping will depend upon the nature of the tan. Dark tans are usually stripped more heavily than paler ones. For ordinary stripping purposes, up to about 4% Borax Decahydrate may be used (based on the wet shaved weight and dissolved in about 10 times its weight of hot water).

6. Scouring

Once removed from the tan liquor, the grain surface of vegetable-tanned leathers often needs cleansing to prevent blooming. Scouring, involves working over the wet with slickers and brushes. The cleaning is greatly assisted by employing a 2% solution of Borax, the alkalinity of which promotes the dissolution of the bloom.

7. Preparation of vegetable tanning liquors

Borax can be used to solubilize crude quebracho and increase its penetrating power. Borax-solubilized quebracho extract is suitable for re-tanning leathers. Chestnut extract can also be freed from insoluble material by addition of 4-5% Borax.

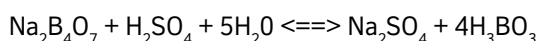
8. Neutralization of chrome leather

Freshly tanned chrome leather is very acid because of the presence of sulfuric acid in chrome tanning liquids. Acid radicals in the leather may directly combine with the collagen (protein-bound acid) or may be associate with the positively charged collagen chromium complex. It is necessary to reduce the acidity of the leather by neutralization before carrying out subsequent treatments, such as dyeing and fat liquoring. The degree of neutralization required depends on the type of leather being made. Good neutralization is desirable for leather which is to be completely dyed and softened. Care must be taken not to raise the pH too high to prevent coarsening of the grain. If the leather is to have some degree of firmness, penetration of the fat liquor must be avoided. This may be attained by leaving the interior somewhat acid. A neutralizing agent requires a solution of which the pH is sufficiently high to allow removal of the protein-bound acid, without affecting the collagen-chromium compound. Both borax and sodium bicarbonate (pH 9.2 and 8.3 respectively) are suitable neutralizing agents. Borax has the advantage of greater stability, particularly if the temperature is raised. Sodium bicarbonate is liable to decompose forming the more alkaline sodium carbonate (pH of N/10 solution, 11.3). Too high a pH leads to over-neutralization. Borax can neutralize

the outer layers of the leather effectively and rapidly while leaving the interior somewhat acid. It is thus preferred for grain leathers which possess smooth grain, good feel and springiness, e.g. box calf and glazed kid. Borax is also preferred for black leathers, greasy skins and it is especially applicable for heavy chrome leathers. It is recommended for neutralizing chrome leather prior to vegetable re-tanning.

Because the exact method of neutralizing will vary with the type of leather, the following is intended only to give a general indication of the procedure to be followed. After tanning, aging and shaving excess salts are removed by washing. The leather is drained and refloated in one and a half to two times its weight of water at a temperature of 45-55°C. The amount of Borax to be used will vary with the substance and type of leather and the degree of neutralization required. Usually 2% based on the shaved weight is adequate added in two or more portions at intervals of 15-30 minutes. After the last addition the drum is stopped and the condition of the leather is inspected using various indicators.

During neutralization, sodium sulfate is formed in the reaction:



To avoid blooming the neutralized leather must be well washed in warm running water. Since washing may further neutralize the pelt it may be desirable to inspect the leather once again. Borax may be used in tanning with other mineral salts - zirconium, iron and aluminum.

9. Leather dressing and finishing

Dried leather requires various additional treatments before it is ready for use. Stripping may be employed as mentioned above, followed by re-tanning, dyeing, fat liquoring or currying, and finishing. During fat liquoring leather is drummed in an oil-in-water emulsion to soften, waterproof and render it more elastic. A fat liquor consists of a blend of oils, water and an emulsifying agent. Mineral, vegetable or animal oils can be used. Borax Decahydrate may be added to adjust the pH and assist the production of stable emulsions.

Currying (scraping) is an alternative method for making leather pliable and waterproof by impregnating it with fats and greases. The grease mixture may contain Borax.

In some types of leather, particularly light leathers where appearance is important, a final finish or season is applied to the surface. Casein and shellac solutions are suitable for filling the grain of the leather, producing a soft, full feel. Casein is employed as the basis for a glaze finishes and imparts a film that is softer than obtained from shellac. Both are used as a binding agent and a film former in water pigmented finishes. Casein-based finishes can be fixed by treatment with formaldehyde, acetic acid or by chromium salts, such as the acetate.

References

More detailed information on Borax and boric acid in leather manufacture can be found in the following references:

H.F. Green and I Mann. *Leather Trades' Review*, 387, May 19th, 1954.

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F.W. Woodroffe, F.G. Caughley and M.E. Pattinson. *J. Soc. Leather Trades Chemists*, 41, 206-216, 1957.

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