



Neutralisation: the key to successful retannage, dyeing and fatliquoring

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The main purpose of the neutralisation process in the production of chrome-tanned leathers is to reduce the acidity throughout the hide or skin structure. This is to enable the retanning, dyeing and fatliquoring processes to be carried out successfully. In chrome leathers, pH values usually range from 3.0 to 4.0, and this is far too acidic to allow penetration of anionic products. Neutralisation increases the leather pH to levels that are generally between pH 4.2 and 6.5. These values depend upon the type of leather being produced, and it is only rarely that higher pH values are employed.

The acidity of wet blue leathers originates from both the acids used in the pickling process, and from the fixation of chrome salts to the collagen. And, because of this acidity, chrome-tanned leathers have a very strong cationic character. In order to carry out retanning, dyeing and fatliquoring, the leather must be de-acidified to reduce the reactivity with process products. As most of these are anionic, this reduced reactivity allows their penetration and diffusion into the deepest layers within the leather structure.

The neutralisation process

The first step in the process is usually a wash. This helps to re-hydrate the leather, remove the dust left behind by the shaving operation, and remove some of the free acids from within the structure.

This wash also plays an important role as it eliminates non-fixed chrome salts from the neutralising bath, as these may react with the neutralisation products and create insoluble chrome precipitates. If this occurs, these precipitates form within the outer layers of the hides—that is the grain and flesh sides—hardening the leather and leading to chrome stains. These subsequently acquire an intense colouration in dyeing, and so can affect the evenness of the dyeing. The softness can also be jeopardised.

As a second stage, the actual pH adjustment is carried out using neutralising agents. When complete, a final wash removes the soluble neutral salts formed by the neutralising reaction. Generally, the removal of these salts is desirable as they can both increase the hygroscopicity of the leather, and affect the handle by making the leather feel heavier. Moreover, these neutral salts are not bound within the leather structure, so they may cause saline migration to the surface of the leather. This can cause unsightly salt spues and irregular grain swelling on finishing which affects both the physical properties of the finish and the uniformity of uptake.

Neutralising agents

The choice of neutralisers depends on the type of leather that is being produced and the pH that has to be achieved.

Products that are only slightly alkaline neutralise the free strong acids in the leather and form soluble salts, and these are easily removed by washing after the neutralising stage. Sodium bicarbonate is a typical product, but tends to carry out a superficial neutralisation and can only penetrate into the deepest layers of the structure with difficulty. This happens because strong ionic links are formed with the free sulfuric acid which lies immediately on the surface, and this blocks the penetration of more neutralising molecules. Moreover, these salts can also react with acid groups in the leather, further restricting neutralisation to the outer layers, so the inner layers can remain extremely acid.

Chemicals that are both alkaline and provide a complexing action have both the ability to neutralise free strong acids and to combine with protein-linked chrome molecules to form complexes. Sodium salts of organic acids, polyphosphates and sodium sulfite behave in this way.

These neutralisers react with free sulphuric acid to form more volatile acids and soluble salts, which can then be easily eliminated in washings. But, they also form links with protein acid groups and, where they are monovalent, aid the penetration of more molecules into the structure of the hides. This promotes a faster and deeper neutralisation.

Some types of neutralising agent also have buffering and dispersing power. These effects prevent sudden pH changes in the process, and can be considered safer to use. This is because fast pH change can reduce the physical strength of the fibres, or cause loose grain due to hydrolysis of the protein throughout the structure.

The buffering component allows the float/leather system to undergo a slow increase in its pH value, coupled with good penetration to remove acidity from the inner layers. Accordingly, this avoids damage to the fibre structure.

The dispersing effect is of value later as it assists the dispersion and penetration of the retanning agents and especially the dyestuffs. This produces more uniform dyeings, higher dyestuff yield, and a more even colour of the grain surface when compared with the flesh side of the leather.

Process conditions and controls

As with all stages of the leather-making process, neutralisation requires careful control.

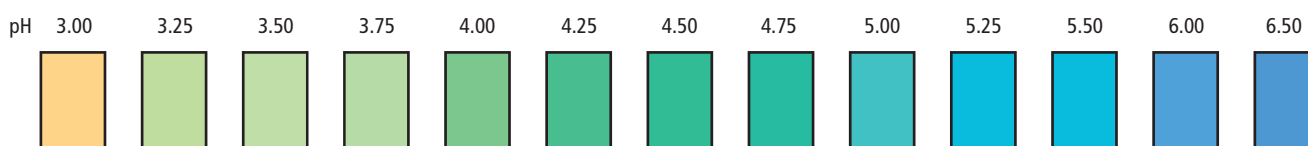
pH CONTROL

As the objective of neutralisation is to reduce the acid load in the leather, the pH can be considered a direct indicator of the neutralisation process. The pH of the float is checked with a pH meter, while the pH throughout the leather section is checked using a Bromocresol Green indicator. This is in the form of a ►



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Panel 1: Colouration of Bromocresol green indicator at various pH values



* pH bands closer to 5.0 may also be checked with bromophenol blue

solution, and is spotted onto a fresh cut in the leather. Different colours then develop depending on the pH of the leather throughout the section, as illustrated in *Panel 1*.

The pH band required is dependent upon the properties of the leathers being produced, and is mainly related to the softness and type of touch required. Usually, to obtain firmer leathers, neutralisation must be milder—that is, around pH 4.5. For softer results, the neutralisation must be kept closer to the neutral band; that is, the pH may rise to around 6.5. However, the main factor for success is for the neutralisation to be uniform throughout the whole thickness of the leather to the required value. Leathers that are not evenly neutralised from the outer layers through to the deepest areas will never be uniformly retanned, dyed or fatliquored.

THE FLOAT VOLUME

The float volume is very important so that any salts formed may be fully dissolved, and the leather becomes perfectly rehydrated. If the leathers have lost too much water at the wet blue stage, it is recommended that neutralisation is carried out in two stages, either by changing the float for a new one, or by leaving the leather in the neutralising float for longer.

THE PROCESS TIME

The time for neutralisation is directly related to the thickness of the leather; the level of rehydration of leathers if they have dried out when in the wet blue state; and the process temperature. It is very important to ensure that the time for neutralisation is sufficient to achieve neutralisation across the whole thickness of the leather. The properties of the neutralising agents used directly influences the rate of penetration, and the balance between the pH within the leather and the bath, until they become stabilised at the same value.

THE TEMPERATURE OF NEUTRALISATION

Temperatures higher than 35°C must be avoided otherwise the rate of reactivity may be increased and there is a danger of precipitates forming on the surface of the leathers. In addition, some neutralising agents—such as sodium or ammonia bicarbonate—may decompose at high temperatures, causing a sudden increase in the pH of the system.

Synergistic neutralising agents

Different neutralising agents used alone in a balanced

combination, or with basic chemicals such as sodium formate or bicarbonate, may generate very different and interesting synergetic effects. When applied correctly, leathers can be processed more safely, and with better neutralisation ensured.

These blends are created according to the effects required from neutralisation, and the desired properties of the final leathers. The characteristics and use of neutralising agents, which cover most of these needs, are given in *Panel 2*.

Panel 2: Synergetic neutralising agents

Composition	Main Characteristics
Organic alkaline salts with complexing effect ⁽¹⁾	➤ Excellent buffering power ➤ Mild, deep neutralisation ➤ White leather lightening ➤ Facilitates penetration and distribution of retanning agents
Polyphosphates ⁽²⁾	➤ High complexing effect ➤ Dispersing effect on vegetable tannins ➤ Facilitates penetration of retanning agents and dyestuffs
Neutralising tannin with retanning effect ⁽³⁾	➤ Excellent buffering power ➤ Mild neutralising and retanning effect ➤ Natural tanning dispersant
Neutralising tannin with dispersing effect ⁽⁴⁾	➤ Excellent buffering power ➤ Dispersing effect on natural tannins ➤ Dispersing effect on dyestuffs. ➤ Facilitates penetration and equalisation

The neutralising process may appear to be simple, but it demands a lot of attention, particularly with regards to the handling care of wet blue leather, the choice of products to meet the final leather requirements and the control of the process. If careful attention is taken, however, the optimum results can be gained from retanning, dyeing and fatliquoring to ensure the best characteristics in the final leather. 

Legend

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