

Masking in leathermaking

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The principle of using a chemical to counteract some of the reactive effects that the collagen may have is known as masking. For many years, tanners have used the principle of masking to reduce the reactivity of the vegetable tanning agents, which have started causing drawn effects when highly concentrated vegetable extracts are added during tanning. The masking may also take place on the chemical that has an astringent effect with the leather, see Figure 1.

Chromium tanning

In the early 1900s, the tanners who were moving over from a two-bath chromium tannage into a single bath chromium (III) system, found that neutral salts, which had a position higher in the Hoffmeister series than NaCl, enhanced the penetration of the chromium salts into leather, especially into very thick steer hides. In 1916, student John Wilson together with Henry Procter realised that as you use sugar to reduce the chromium from dichromate into a trivalent form, and added that mixture to the leather, the remaining sugars with their hydroxy groups helped increase the penetration and resulting fixation. The leathers were profoundly superior to their unmasked counterparts. McLaughlin and Theis (1945) defined the masking of chromium as a system that alters:

- The composition of the chromium complex
- The electrical migration of the chromium
- The pH value of the liquor
- The ability of the chromium liquor to resist alkali

It needs to be remembered that this definition, and similar ones since, refers to glucose-reduced liquors that are generally aged and are truly masked. That is, the reaction between the masking

agent and the chromium complex have been given time to complete. Many of the published research papers in the 1930s to 1970s speak about the penetration efficacy of glucose-reduced chromium salts.

Modern chromium salts are generally reduced using sulphur dioxide to become chromium sulphate. The addition of a separate 'masking agent' is performed during the pickling operation and, after addition of the chromium sulphate in that pickle, the time for a chemical reaction between the chromium and the organic ion is minimal. Some tanneries add the masking agent with the chromium in the tan bath, reducing the possible masking time even further. Covington (2009) gives the relative increase in chromium uptake (if unmasked chromium is 1.00) as 1.06 for formate and 1.18 for acetate, which may be construed possibly as a marginal effect for chromium exhaustion. From a reaction perspective, one would have to agree with the rationale.

However, tanners know that by the end of the tannage the composition of the chromium complex has been changed and that the overall penetration and benefit of using a masking agent outweigh the benefit without using them. In the beginning of the chromium addition, there is probably very little reaction. If anything, the chromium may even be more reactive.

So why do formate-masked tannages give fuller leathers that

have a finer grain pattern? It is probably linked with the very nature that it does not do a full masking. In the beginning, the formate does not have the time to react with the chromium and has already fully penetrated through the hide/skin (as it was possibly added in the pickle). When the chromium is added, there is a period where the chromium reacts, a little, with the leather. The pH is low and so is the affinity of the chromium for the fibre.

As the chromium penetrates the leather, given the usual pickling time – 60 to 90 minutes, the formate will react with it. As passage into the leather progresses, it will encounter a slightly higher pH than the surfaces of the leather, particularly with thicker cattle hides. It is here where the formate comes into its own; as a masking agent, it will prevent the chromium from becoming a higher basicity. It will increase the precipitation resistance of the complex. In other words, a tanner must add more alkali to get a greater basicity in the chromium complex. It is not uncommon for unmasked tannage to reach higher basicities in chromium baths at pH 3.8 compared to

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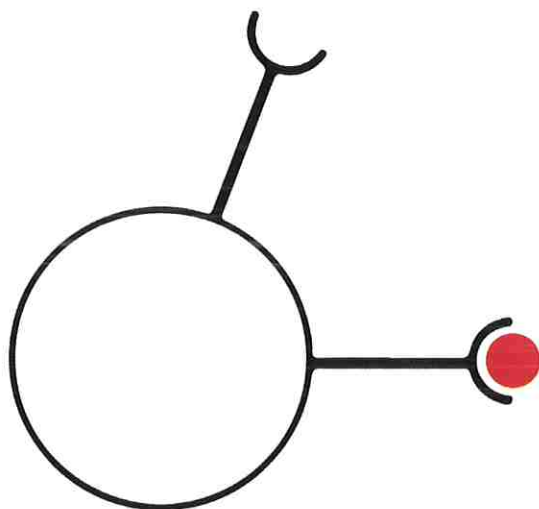


Figure 1. Schematically, the diagram shows the red-coloured “chemicals” interacting with either the collagen or the astringent chemical itself, slowing their chemical reaction.

masked tannages that have the same basicities at pH 4.2. Higher basicity at lower pH is detrimental to chromium complex stability and can result in uneven distribution and more precipitation.

The use of sodium formate or formic acid will help with the control of reactivity of the chromium complex; maybe not at the start of chromium tannage but particularly at the end, and especially during basification. The chromium-formate complexation can also provide an increased resistance to pH changes. Rapid pH fluctuation is not uncommon in the basification of chromium tannages. A carboxylate salt helps resist these pH variations.

Vegetable tannage

In a completely different approach, the reduction of surface reactivity of vegetable tanned leathers has taken a different chemical path. Binding sites on the surface of the pickled pelt can be conditioned using a hygroscopic salt, such as sodium sulphate, that not only masks surface reactivity but also retains water in the leather surface layers. This water retention is often vital to maintain hydration levels of the leather surface when the grain is exposed to highly concentrated tanning liquors. Concentrates have a high osmotic potential and can draw water away from the leather causing shrinking events. This water loss compounds the penetration problem of the tanning agent into the leather. Why compound? Well, the tannins will be very keen to interact with

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peptide groups on the surface collagen. Hydrogen bonding is independent of pH and most of the binding reaction is easy unless the peptide groups are shielded by the masking materials.

Of course, there are some electrostatic attractions between the vegetable tanning agent and the leather surface (especially in bisulfited extracts) and the addition of chemicals such as sodium hexa-meta-phosphate (Calgon) can slow down rates of tannin reaction. With

careful water control and shielding the extract has no choice but to penetrate the leather substructure.

Dispersion

Dispersal mechanisms of chemicals prone to agglomeration can also be a vital chemical treatment that is required in the tanning bath; to assist with penetration or levelling. Chemicals that aggregate due to electrostatic or hydrophobic effects may need help with keeping separate. The masking associated with the chemical itself (shown in Figure 1) is a schematic representation of what a chemical, like polyglycol ether, would do when interacting with a dyestuff. The dyestuff in question may be prone to natural association with itself or it may be inclined to aggregate because of the process conditions. Polyglycol ethers, such as a fatty amine polyglycol ether, can mask the binding of the chemicals between themselves, forcing the chemical to have a lower molecular weight. A typical chemical structure for a generic polyglycol ether is shown in Figure 2.

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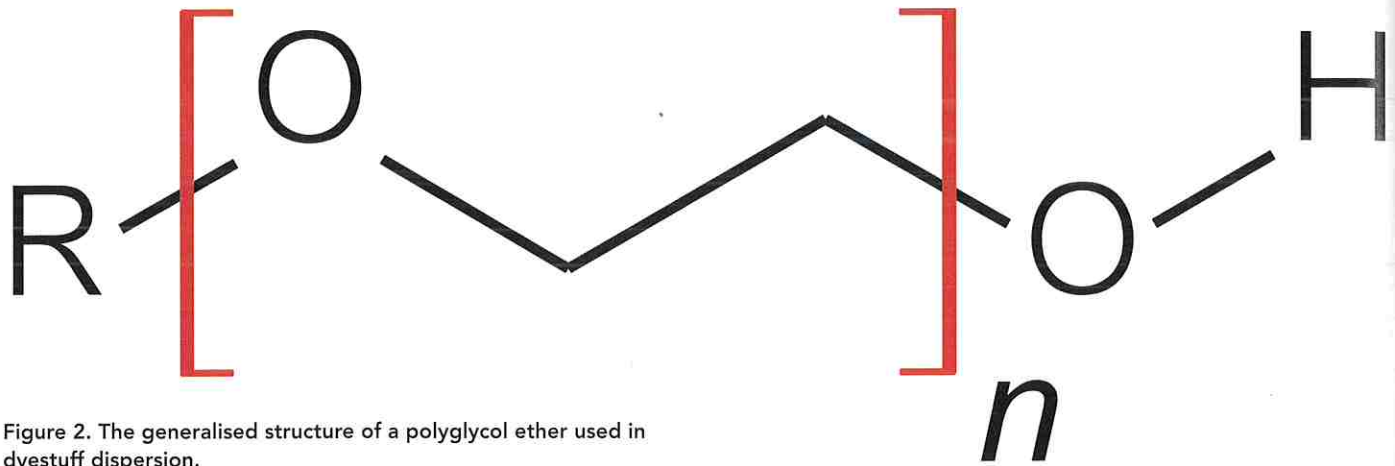


Figure 2. The generalised structure of a polyglycol ether used in dyestuff dispersion.

Some dispersing chemistry relies on a chemical that can do both masking functions shown in Figure 1. The masking agent will react with the chemical that is trying to penetrate the leather and it reacts with the collagen to reduce binding astringency. Polyethylene oxide chains can do a dual masking function. At low concentration the product may have a lightening effect on the dye intensity, but as the concentration is increased the leather colour is normalised, sometimes even intensified.

Neutralising syntans

The use of a synthetic auxiliary has been used on chromium tanned leathers for well over 50 years. These anionic products, often based on naphthalene sulfonate, phenol sulfonates, or lignin sulfonates, see Figure 3, will bind (temporarily) with the collagen. Some of the neutralising agent may bind a little more permanently than what the tanner desires - this gives rise to a bleaching effect, so the tanner should exercise caution when using bleaching products on leathers that require a high dye intensity.

The chemicals shown in Figure 3 can be used as their salt (a neutral form) or as their acids (generally low pH that can make them a little more astringent). Finding the right blend or type of masking agent that is suitable for the leather in question is vital. For

example, when masking a water-resistant leather, using a neutral form of the masking agent will generally help in preventing a loss of dynamic water resistance. If a naphthalene is used, particularly high astringency types, breakdown products or residual monomer of the masking agents must be screened for, as naphthalene (without, for example, the sulfonate group polycyclic aromatic hydrocarbon - PAH), phenol, and formaldehyde are generally included on restricted substance lists.

In some instances, the chemicals shown in Figure 3 can interact with the vegetable tanning materials or the synthetic tanning materials themselves and will improve their solubility and will also mask the collagen and give better penetration.

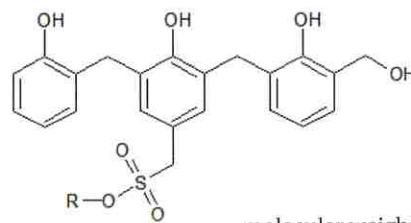
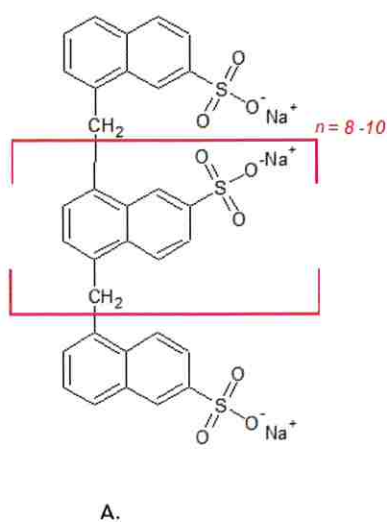
In post tanning, the masking agents are usually added as auxiliaries added together with the neutralising salts (sodium formate, sodium bicarbonate) in the neutralisation step. If the masking agents are added to help dye or retanning agent penetration, then the product can be added 10-15 minutes before the dye itself is added. Sometimes the polyglycol ethers are added when it has been determined that the dye is not penetrating as it should, as a booster to increase penetration speed. Checking of the product penetration should thus be done in a pro-active manner before the end of the dye penetration time, so that a pre-emptive

addition can be made before the end of the allocated cycle time.

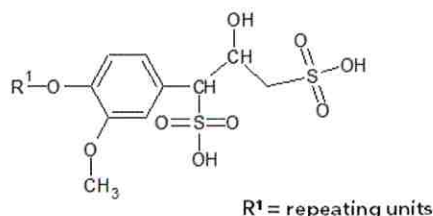
The masking agents are often used as pre-tanning materials that together with a small amount of tanning agent can help and colour the surface. The surface will receive more than a little colour, in that the combination of low tanning agent concentration and masking agent help to place low

molecular weight tannins on the grain, reducing the grain reactivity to the main tannage and effectively masking the surface for additions of other chemicals to follow. Pre-tanning is a slightly more permanent mask but it allows mellow, flat-grained leathers that provide very little problems later.

In general, the concept of masking shown illustrates the versatility of the masking agents to be used as a tool in assisting rapid and even penetration of a range of chemicals that would usually give us penetration problems. ■



B.
R = H, Na



C.

Figure 3. The chemical structures typical masking agents that will bind with the collagen A. Naphthalene sulfonate condensates. B. Phenol sulfonate condensates. C. Lignin sulfonate polymer.

References: Covington, A.D. (2009) Tanning chemistry – the science of leather. RSC publishing, Cambridge, UK.

McLaughlin, G.D. and Theis, E.R. (1945) The chemistry of leather manufacture. Reinhold Publishing Corporation, New York, USA.