Managing Chrome in Leather Manufacture*

by

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Abstract

Chrome Tanning, being still the most used tanning method, has been challenged more and more in the recent past. The main reasons were questions of sustainability and the fact that chromium VI can be formed in leathers tanned with chromium III compounds. From a technical point of view, many solutions exist for using the chrome tanning agent in a most economical and ecological way. In this paper another way is shown for maximizing the distribution of chromium in the cross section of the hide as well as the exhaustion of chromium from tanning float, thus reducing the total chromium emission into the environment. Also the leaching of chrome from wet blue during retanning operations will be considered. The type of chemicals used and the process conditions play an important role in this regard, as well as the type of chrome tannage used to manufacture the wet blue. Various measures and solutions will be discussed in this presentation. The role of chromium VI in tanning is looked at with special attention to the real risks associated with it. Finally the formation of chromium VI will be discussed as well as methods to prevent its formation. A new additive (anti oxidant), which is able to eliminate existing chromium VI and reduce the likelihood of reformation, will be introduced.

Resumen

El curtido al cromo, siendo todavía el método de curtido más utilizado, ha sido más y más retado recientemente. Las mayores objeciones que surgen, son preguntas acerca de la sustentabilidad y el hecho que Cromo VI podría formarse en cueros curtidos con compuestos de cromo trivalente. Desde un punto de vista técnico, muchas soluciones existen utilizando agentes curtientes al cromo con un máximo de beneficios económicos y ecológicos. En este trabajo, otra forma es demostrada que maximiza la distribución a través del corte así cómo también el agotamiento del cromo en el baño del curtido, de manera tal de reducir la emisión total del cromo al medio ambiente. También la indeseada extracción del cromo en las operaciones del recurtido será considerada. Los tipos de productos químicos utilizados y las condiciones de proceso juegan un importante papel en este contexto, así cómo el curtido inicial al cromo empleado en la fabricación del "wet-blue". Varias medidas y soluciones serán discutidas en esta presentación. El papel del cromo hexavalente en el curtido es examinado con especial atención a los riesgos reales asociados. Finalmente la formación de Cromo VI será discutida, cómo también métodos para evitar su formación. Un novedoso aditivo (anti-oxidante, capaz de eliminar cromo más seis y evitar su re-formación será presentado.

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INTRODUCTION

Today approximately 80% of total tanning is based on chromium. Although many alternatives have been studied and do exist chrome tanning with a more than 100 year success story still offers significant economic and technical advantages which can not be ignored and still make it the preferred way of tanning hides. Chrome tanning is very versatile: Wet Blue as an intermediate can be easily stored and traded and then turned into a variety of leather types with very different characteristics as to performance and aesthetics. With the efforts minimizing resources and emissions we will see in future an increasing trend towards processing the hides in the country where they are originating from, at least to an intermediate stage where wet blue still plays an important role.

When it comes to managing chrome in the tanning three main challenges need to be addressed

1. Reduction of emissions of chromium into the environment

2. Re-use of chromium, sustainability of chrome tanning

3. Elimination of risks of chromium VI

Emission of Chromium into the Environment

Fig. 1 shows the different pathways of chromium into the environment. By average, 60 000 tons of pure chromium are being used for leather manufacturing per year. The majority of it more than 90% is entering the environment as leather and leather craps and cuttings. Only a small percentage is deposed of as sludge. Depending on chrome content the sludge goes to regular landfills or on special sites. Sludge can be also incinerated under inert gas conditions at lower temperature to prevent chromium VI formation. However most of the chrome leather or articles manufactured today is not recycled and ends up in landfills or incineration plants, where chromium VI can be formed as well. Modern scrubber units will eliminate chromium VI from the exhaust gas stream. Chrome tanning would be a sustainable technology if the chromium (which is not renewable!) would be recovered from used leather articles or chromium waste and being re-used again later in production. The reason why it is not done is mainly an economical one. This applies also for technologies where wet blue or leather fibers are being reconstituted by various technologies to a new type of composite leather (e.g. leather board, e-leather).

Technologies which are better exhausting chromium from tanning floats are long known and most are based on the use of dicarboxylic acids (DCA), aldehydes or aluminum in the chrome tanning process. The technologies based on complexing with dicarboxylic acids did not find a real broad introduction into the industry for various reasons. In order to get good exhaustion with DCA's a higher pH and temperature at the end of the tannage is mandatory. This has a negative impact on chromium distribution in the hide section, layout (area yield), grain aspect and intensity of dyeing. Also the precipitation of the residual chrome from the exhausted tanning float is more difficult due to the strong masking. Another reason that high chrome exhaustion system did not prevail is the simple fact that a high exhaustion of the chrome float is not needed if the chrome is precipitated from the spent tanning float and used again. Only those tanneries which do not recycle the chrome from spent liquors can see a benefit from a high exhaust system although the amount of chrome left in the liquors after high exhaust tanning is still too high in order to be spent directly into the environment without further treatment. What would be needed is a system with good chrome exhaustion without negatively affecting chrome penetration, and distribution and still achieving good leather quality. The exhausted chromium should be fixed well and washing-out later on should be minimized. Such a chrome tanning process ideally runs with a low astringency keeping the hide in a relaxed stage to ensure good area and cutting yield.

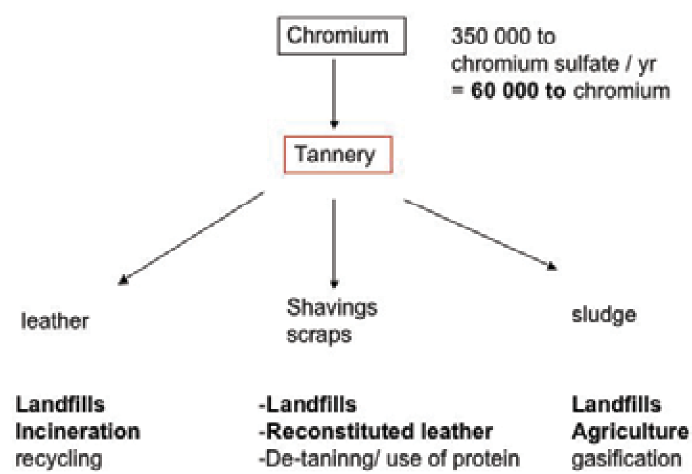

Figure 1. Pathways of chromium: Chromium enters environment in form of leather articles and sludge.

Pickling and Tanning with Polysulphonic Acids (PA)

Interestingly it was found that a special preparation of polysulfonic acids (PA) (Fig. 2) when used in pickling has a positive effect on chrome penetration / distribution and in particular on exhaustion and fixation of the chrome in wet blue. The PA product interacts with the collagen matrix by decoupling the saline links between carboxyl and amino groups. The PA anion attaches to the amino function and thus gradually freeing up the remaining carboxyl groups and making them better accessible to chrome binding. As opposed to the high exhaust tanning made with carboxylic acids the PA anion is not much involved in the complexing reaction with chromium. The chromium exhaustion of PA based tannages thus is less dependent on achieving high pH and temperature at the end of tanning.

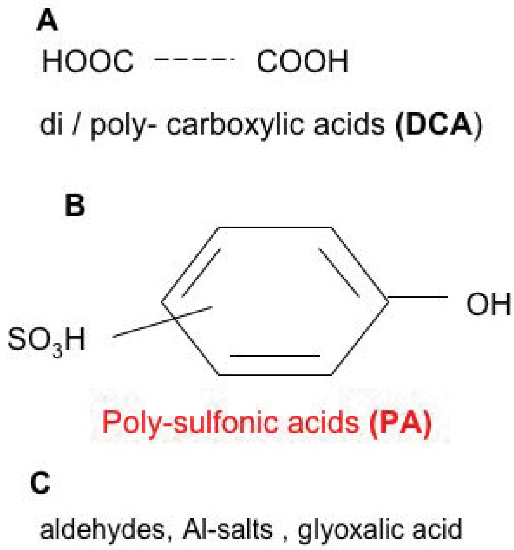

Figure 2. Chemicals used for high exhaustion chrome tanning.

Some figures on exhaustion of different high chrome exhaust systems are shown in Fig 3. The comparison was made on full substance hides by basifying all systems to the same final pH of 3.7-3.8 and temperature of 38-40^0 C. The chrome exhaustion in case of polysulfoniic acid (PA) is superior and not further improved if dicarboxylic acids or polyacrylic acid based polymers were being co-used with the PA..

The typical application of the PA product is the so called 'enhanced' pickling process, where at a Bè of 6-7 the sulphuric acid as well as the chrome offer are reduced and the use of formic acid is eliminated (Fig. 4). Due to the fact that the PA product has a good conditioning and stabilizing effect on collagen the offer of salt in pickle can be cut almost into half. In this 'low salt' process a Bé between 4 and 5 is targeted. And the offer of chromium is reduced by 20% while the chromium content in wet blue is maintained. In both processes a significant reduction of chrome (50%), sulphate (40%) and chloride (50%) in the waste water is possible. The savings on chrome offer however is only a benefit if the chromium in residual tanning float is not recycled.

Another interesting fact is the influence of the PA product on chrome penetration. PA as an acid is penetrating the pelt not as fast as a regular pickle with formic and sulphuric acid would do, but it can be greatly enhanced by adding a small amount of chrome along with it (Fig.5a). A pickle overnight was run (equilibrium pickle) to proof the fact that the polysulphonic acid basically gives a faster penetration of the chrome. This is mainly visible during the first two hours after the addition of chrome. In a regular pickle of 4-5 hours these differences go away (Fig. 5b). The fact that basicity in the center of the hide is higher in case PA is used as a pickle acid explains the effect that chrome content in center of the hide is slightly higher,

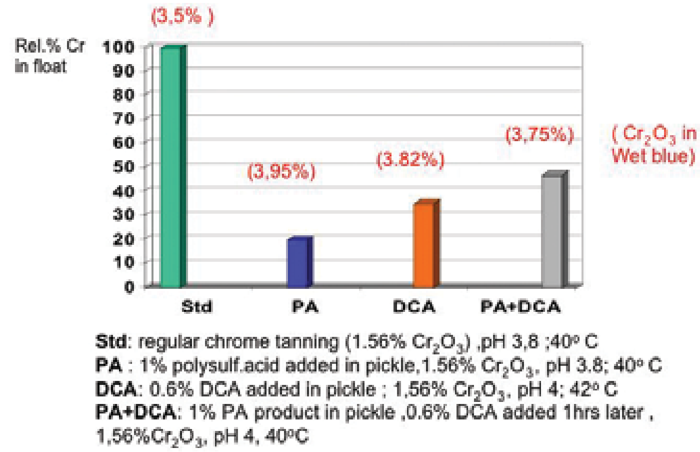

Figure 3. Chromium uptake with polysulfonic acid (PA).

Another area to look at is how well the chrome is being fixed in wet blue. A wet blue made with the polysulfonic acid will release less chrome in the first wash or wetting back of the wet blue. Various tests at tanneries confirmed the improved chrome exhaustion and fixation with polysulfonic acid pickling. This fact is also reflected in improved physical mechanical properties of the crust leathers made with the new tannage (Fig 6). Crust leathers are very well laid out, have an even and fine grain and fuller flanks resulting in better cutting yield.In many cases the chrome retannage can be eliminated and the penetration of retanning chemicals and dyestuffs was improved. The dyeing is more level and the white zone often observed under the grain disappeared.

Chromium Exhaustion and Fixation in the Wet-end Processes

Apart from the chromium emission coming from main tanning process chromium can be leached throughout the wet end processes. In case of chrome retanning this amount can even be more significant. Understanding the factors, which have an impact on chrome leaching helps to design an optimized wet end process. The most important factor plays the olation process. The older the wet blue the less chrome will be leached out. The nature of retanning chemicals is also important. Depending on how strongly a retanning product, like a polymer, syntan, fat liquor, acid or emulsifier, competes with the collagen carboxyl groups for the binding sites of chromium, more or less chromium will be set free (Fig. 7)

Washing wet-blue is the first problematic step since it releases most of the unbound chromium depending on degree of olation (aging) and type of chrome tanning. Adding a dual functional emulsifier [(3)]* without additional acid supports chrome fixation, especially on wet blue produced with the polysulphonic acids. [(1)] Re-chroming should be avoided or minimized which is possible on polysulfonic acid based chrome tannages. For articles where re-chroming is necessary

*Editor Note: All the superscripts in this manuscript [i.e. (3)] refer to appended product identification glossary.

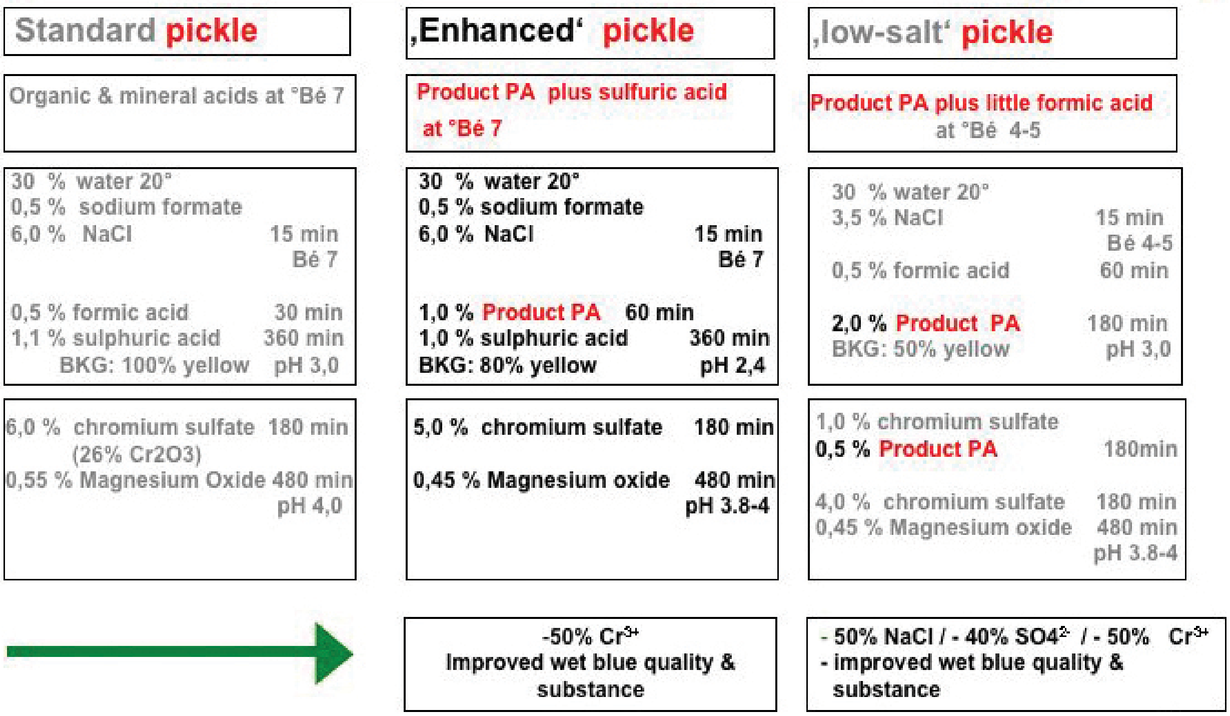

Figure 4. Pickling and tanning with PA on full substance hides.

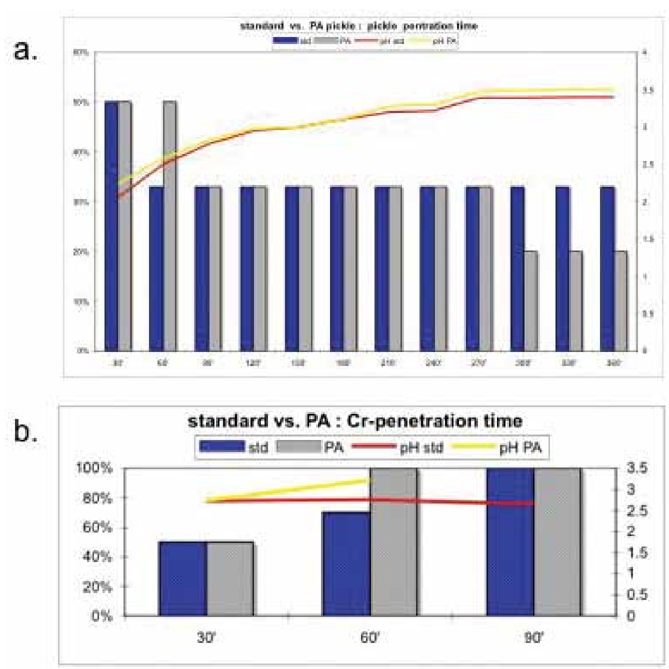

Figure 5. Penetration of pickle & chrome.

it can be partly or fully replaced by using specific polymers [2,4] and modified glutaraldehyde products [5,6] which indirectly improve the affinity of chrome to the collagen matrix and greatly reducing the amount of leached chromium.

In a re-chroming process the neutralization is the main process step influencing chromium fixation. Using above mentioned polymers in re-chroming [2,4] before neutralization increases the

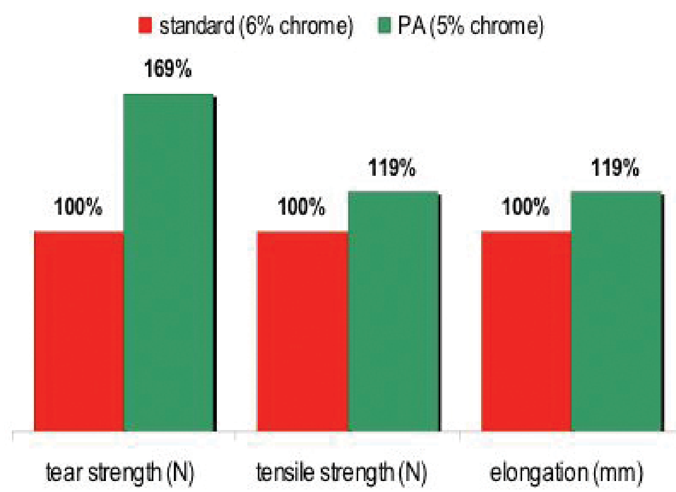

Figure 6. Phys.mech. properties of leathers made with PA product.

chrome fixation by up to 70% (Fig. 8). In regular retanning processes especially glutaraldehyde based products, if once activated at a higher pH, have a positive effect on the fixation of chromium. It is therefore recommended to apply them before neutralization, allowing full penetration before the pH is increased with special neutralizing [7] or basifying [8] agents.

Compared to common processes, where the neutralization is done in a separate bath, the fixation of chromium can be significantly improved by performing neutralization, re-tanning, dyeing and fixation all in one bath using above

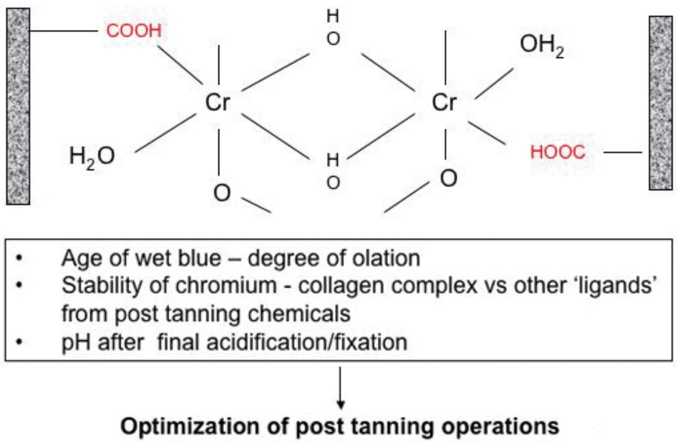

Figure 7. Chrome fixation and leaching.

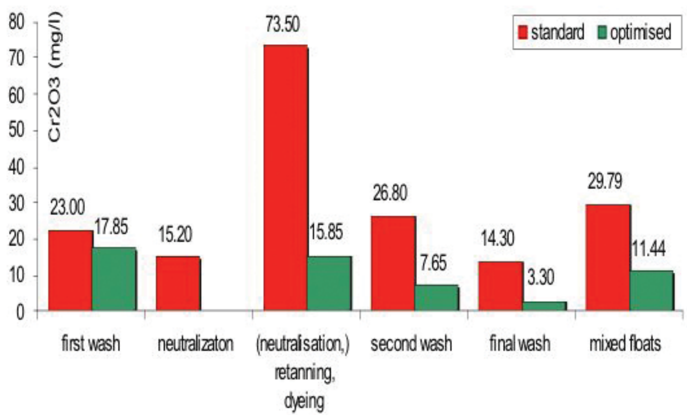

Figure 8. chromium in spend wet-end floats of an optimised "one bath" process.

mentioned measures. The benefits are easier processing and the possibility to reduce total water consumption.

The role of fatliquoring in the fixation of chromium is often underestimated. Especially waterproofing fatliquors [9, 10, 11] can react with unfixed chromium of the wet blue or in the retanning bath and are thus are a preferred choice reducing chromium leaching when it comes to selecting the best fat liquors.

The final acidification of the retanning, dyeing and fatliquoring bath is the most contra productive step if it comes to chrome fixation. On one side anionic products need to be fixed by lowering the pH with acid and on the other side low pH-values respectively acids trigger the release of bound chrome from the leather. For this reason acidification needs to be carried out with care. The use of the polysulfonic acid product [1] helps a great deal to avoid chromium-stripping when used for fixation at the end of the process particularly if a special formaldehyde-free cationic fixing agent [12] is added after the acidification. Thus the amount of acid (here PA product) can be lowered to reduce chrome stripping.

When all of above measurements are being applied it is possible to reduce the amount of chromium leached during wet end operations up to 70%. What is interesting it also helps to reduce the leachable chrome from final crust leather and to pass the chrome leaching test (treatment with a solution of artificial sweat) as asked by some brands and eco labels. (Fig. 9) However when putting things in perspective we can say that chrome emissions from wet end operations compared to those from main tanning play a much inferior role unless a full chrome retanning is done (which often is not needed particularly if the tanning is done with PA product).

Strategies for Treating Chrome Containing Waste Floats

As a matter of fact none high chromium exhaustion tannage (also not the one conducted with the new PA product) is able to exhaust chrome to levels of a few ppm to have the waste water sent directly into streams or municipal waste water treatment plants (Fig. 9). A high exhaust tannage is particularly suited for these tanneries which for some reasons do not want to precipitate chrome from main tanning floats but rather mix it with the retanning floats where either a final precipitation is done or the combined floats after cleaning be used in various washing steps in retanning by applying a counter flow principle. The most common way is the precipitation of chromium after main tannage and re-use of the chrome together with virgin chrome in next tanning cycle. An interesting, alternative method is recycling of the residual chrome tanning float (from main chrome tannage) in a counter stream principle: The exhausted chrome float is cleared from fibers and fat and then after adjusting of Bé used in pickle, the ex pickle float is collected as well and used as 2nd wash after bating which is a kind of pre-conditioning step. The chrome tannage is always started with fresh water. The goal is to fix maximum amount of chrome in the leather and reduce the amount of chromium ending up in any kind of sludge to a minimum.

Chromium Toxicity, Prevention of Chromium (VI) in the Wet End

Chromium (III) compounds as soluble salts are classified as 'harmful to aquatic organism and may cause long-term adverse effects in an aquatic environment, they do not have an acute toxicity profile. In sludge or leather waste where pH is usually 7 or higher chromium (III) is present at a higher basicity stage (eventually Cr-hydroxide resp. Cr-oxide) where it is fixed very well and not mobile. Even if chrome (III) containing waste water would be released directly to the environment the Chromium (III) is bound to soil and immobilized, oxidation of chromium (III) to Cr VI in soil / sludge does not occur.

Chromium (VI) is toxic to humans if swallowed or inhaled (fly ash, mist, etc.). If skin is repetitively exposed to chromium VI sensitizing will occur causing allergies and skin irritations. The health risk with leather is limited to skin contact as chromium (VI) would never be able to enter the body either

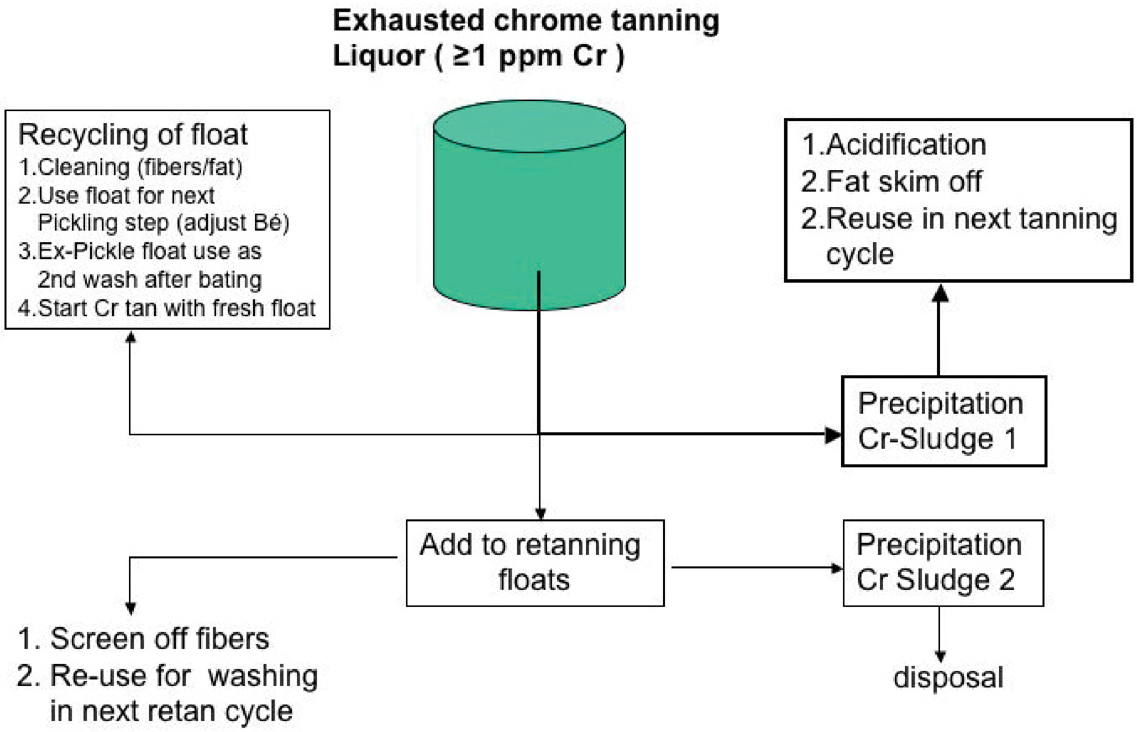

Figure 9. Exhausted tanning liquors.

via skin or by inhalation. In case of skin contact (sweat) the chromium VI would not be stable but be reduced to chromium (III) and immobilized at the collagen. There is no clear evidence in any study where skin irritation (allergy) of a patient could be clearly and unanimously related to the chromium VI content in leather. Studies which tried to proof this fact have no reference to tests which showed that respective leathers were tested for the absence of other potential allergens, like e.g. DMF (diemethylfumarate) commonly used to preserve leathers during storage or shipping. Usually the levels of chromium (VI) in leather are very low (less than 10 ppm) or absent and there is very little health risk, if at all. According to the German Ministry for Environment an allergen is of high concern if more than 1% of people get sensitized. There is neither study nor proof that such a percentage of people in contact with leathers were sensitized. Regardless of those facts the goal must be to eliminate the formation and presence of chromium VI in leather, especially since there were cases where higher amounts (70 – 80 ppm) of chromium (VI) were found in working gloves and garments, but also in shoes.

Leather manufacturers, brands, testing labels as well as legislators of various countries have limits on how much chromium (VI) they allow to be present in leather articles. Some legislators and many eco labels and brands have settled on an allowable limit of not more than 3 ppm (which is basically the detection limit fro chromium VI)

How can we prevent the formation of chromium (6+) in leather and/or leather production? At low pH chromium (VI) is unstable and a high pH favors chromium (VI) formation. Under the conditions of chrome tanning and in wet blue chromium (VI) is not stable and not present. Neutralizing agents (sodium formate, sodium bicarbonate) have little effect on chromium (VI) formation; phenolic syntans and glutaraldehyde [5,6] have even some preventive effect. Vegetable tannins of any kind have a good preventive effect but can change the leather color; Tara is considered to be most effective followed by Mimosa. High amounts of natural fat due to poor degreasing or the presence of fatliquors with high amounts of natural oils (unsaturated fats) have a quite negative effect and can form significant levels of chromium (VI) especially in the presence of heat, light and low humidity. Synthetic fatliquors or polymers are favorable. Good degreasing during beaming operations is highly recommended.[13,14]

Ammonia used for dye penetration also favors the formation of chromium (VI). In the past years the demand for heavy oiled and waxed leathers has increased. It has been found that application of unsaturated waxes and oils e.g. neat foot oil based products in oil finishing operations can provoke the formation of chromium (VI) in leather even if the crust leather as such shows no presence of chromium (VI). The most efficient way to eliminate or to prevent the formation of chromium (VI) even under harsh conditions is the use of special antioxidants.[15] They contain a penetrator which helps to better distribute the product in the hide cross section and

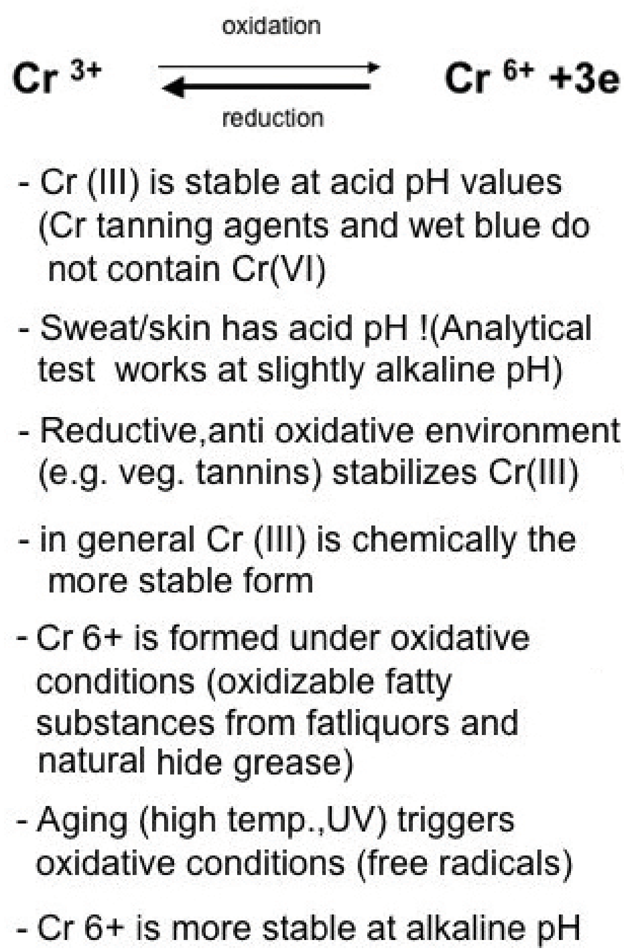

Figure 10. Chromium (VI) formation and prevention.

supporting more consistent analytical chrome VI testing results. Compared to ascorbic acid they do not form a brownish discoloration when exposed to light and air and can also be used in post treatment operation of leather, which has too high amounts of chromium (VI). The antioxidant product is best used in a last separate processing step during wet end operations, where it should be applied in sufficient amounts in a short float with no subsequent washing. Leathers treated this way usually will pass the chromium (VI) tests when done on leathers after aging. The same application can also be used as a preventive measure in order to ensure that leathers will pass the chromium VI tests. In any event the most preferred way is to avoid the conditions during processing which trigger chromium VI formation that is namely the presence of unsaturated fats and oxidizing agents.

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PRODUCT GLOSSARY

1. SELLATAN® PA liq.
2. MAGNOPAL® SFT-F
3. BORRON® WP
4. MAGNOPAL® FTP
5. SELLATAN® CF
6. SELLATAN® WL-G liq.
7. SELLASOL® SF
8. CROMENO® MFN-1
9. DRYWALK® FAT
10. DRYWALK® WAS-1
11. DRYWALK® SIL
12. SELLA® FIX HPF conc.
13. BORRON® DN
14. BORRON® SE
15. SELLASOL® C6
16. CORIPOL® DX 1202