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FORMATION, PREVENTION & DETERMINATION OF Cr(VI) IN LEATHER

A short overview of recent publications

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1. Introduction

The Technical Report entitled “Sources, Detection and Avoidance of Hexavalent Chromium in Leather and Leather Products” prepared in August 1999 (15) summarized findings from the research work carried out at LGR, Germany and some results of Cr(VI) determination in various types of leathers collected from several tanneries in India. In the meantime several researchers and institutes published a lot of work. The purpose of this paper is to provide, as a supplement, a short overview of recently published articles in international leather magazines on this highly important and sensitive issue.

2. Formation of Cr(VI) in leather

2.1. The main findings of the investigations carried out at LGR, Germany (6) on a possible formation and avoidance of chromate in leather were as follows:

- A close connection between the pH-values of the neutralisation float and the Cr(VI) content of the leather could not be established.
- The use of a wetting auxiliary with reducing abilities prior to the dyeing could not avoid in some cases the Cr(VI) formation under drastic conditions like heating at 80°C.
- Vegetable tanning agents like wattle, quebracho, chestnut and tara play a very important role in avoiding chromate in leather. Especially tara was very effective even using a very low offer.
- Polymers or synthetic retanning agents had neither a negative nor a positive effect.
- Cr(VI) formation in leather is heavily influenced by fatliquors, especially natural products such as fish oils.
- Mechanical processes like vacuum drying or buffing of the leather seem not to contribute to the formation of Cr(VI) in leather.

2.2. **The result of some investigations in Italy** (13) was that no Cr(VI) could be detected after correctly performing the conventional chrome tanning processes, analysed after each processing stage. After thermal treatment and UV radiations high amounts of Cr(VI) were found in the same crust leathers. Experiments using single chemical substances showed that fatliquoring with sulphited fish oils resulted in high Cr(VI) values. Retannage with natural tannins did not support Cr(VI) formation.

2.3. An interesting factor, also observed at LGR, was raised by **D. Graf** in his article (5) dealing with the influence of the relative humidity of air during storage on Cr(VI) in chrome tanned leathers. The author states that Cr(VI) can be formed only if the leather is in contact with atmospheric oxygen, if it is fatliquored with fatliquors containing unsaturated fatty acids and/or natural fat, if these fatliquors are free from anti-oxidants, if less than 4% vegetable retanning agent is used and if the relative humidity of the air is under 35%. People often say that Cr(VI) is developing under storage conditions. LGR rather observed the contrary: during storage the original Cr(VI) content of the leather was lowered. Experiments carried out showed a Cr(VI) content of 48 ppm on 20% rel. hum. which was lowered to <3 ppm on 40% rel. humidity. This agrees with findings from LGR analyses: In most cases higher values of Cr(VI) were detected after heating on 80°C which resulted in about 6% water content than could be detected after UV lightening which resulted in about 10% water content. The findings correlate with the results of Nickolaus (11) who investigated the presence of Cr(VI) in shoe upper leather.

2.4. The influence of photo-ageing (UV lightening) on Cr(VI) formation in leather was investigated by **Font** et al. (4). The following main reasons for a formation of Cr(VI) in originally Cr(VI) free leathers are mentioned: Oxidation by air favoured by high neutralisation or dyeing pH, photo-ageing by air subjected to light, thermal ageing by air subjected to heat. Cr(VI) related to high pH disappeared after washing. UV lightening caused high values and the formation of Cr(VI) was lower with vegetable retanning agents. Tannins do not absorb the UV wavelengths that means that they have the ability of an antioxidant. In experiments some antioxidants like tocopherole were less effective than vegetable tanning agents.

2.5. Saddington (12) deals only with the influence of fatliquors on the Cr(VI) formation. He gives an explanation for the reaction of unsaturated fats with chromium taken from publications. Conditions for the oxidation are in his opinion oxygen, heat, moisture and UV light. Results in other publications show that moisture is not necessary for the Cr(VI) formation, even it has a preventing effect. Radical scavengers added to the fatliqour prevent the reaction with chromium. A patent is published in which anti-oxidants are mentioned with effect against the presence and the formation of Cr(VI) in leather. They forget that normally leather does not contain this substance but it is formed with some fatliquors. The paper does not contain data on the leathers produced, the determination method or the special fatliquors employed in this work.

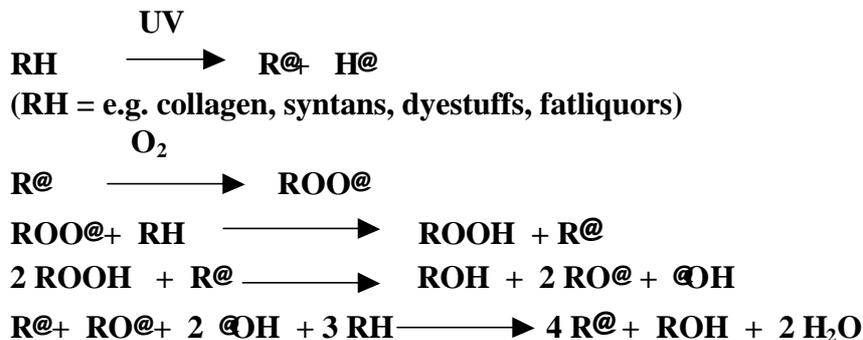
2.6. Wolf (14) emphasises the use of auxiliaries with reducing ability in neutralisation and wetting back before dyeing. There is no new result compared with the work of LGR.

2.7. Nickolaus (10) deals with the effect of glues normally used in shoe production. Alkali glues react faster with the pieces to be connected than acidic ones and that's why shoemakers prefer to employ them. If the original leather sample contained Cr(VI) even in a concentration which cannot be determined exactly (<3 mg/kg) the Cr(VI) amount increased after this process and after dry heating (heat setting). It decreased after several weeks' storage. Wetting the leather resulted in in very low Cr(VI) contents which could be maintained in case of storage in about 100% rel. Hum. One of the observations published is that an extractable Cr(III) content < 50 mg seems to prevent a Cr(VI) formation. This has to be proved with much more analyses, LGR could not find a strong connection.

2.8. Ferreira et al. (2) worked on hexavalent chromium formation during leather combustion. The original leather sample did not contain Cr(VI), heating in the 300-1000°C ranges increased the levels of Cr(VI) in the ash depending on the temperature and the holding time. The leather ashes showed higher Cr(VI) levels for burning temperatures < 500°C and > 800°C. The longer the holding time was the less Cr(VI) was detected.

3. The supposed mechanism of Cr(VI) formation

The supposed mechanism of Cr(VI) formation in leather is explained by several authors (13, 4, 12) without confirming it by experiments. This mechanism is connected with the oxidation of unsaturated fats and can be summarized in the following:



Free radicals are formed by UV light from a molecule whose normal covalent bond was split to create two unstable moieties. These free radicals react with oxygen developing very reactive derivatives such as peroxides, and radicals such as HO^\bullet , LO^\bullet and LOO^\bullet which are strong oxidants. Probably this is the reason for chromium oxidation in light.

After employing fatliquors containing a high amount of free fatty acids yellowing of the leather was observed by **Cory** (1). At the same time the hydrophobic character changed into a hydrophilic one indicating the development of oxidation products from the fatliquor. And these oxidation products are supposed to react with Cr(III) to give Cr(VI).

4. Determination of Cr(VI) in leather

The standard determination methods like DIN 53 314 or IUC-18 are very often criticised because of the high pH (7,5-8,0) of the extraction medium (phosphate buffer). Often it is said that the used buffer solution somehow reacts with Cr(III) so increasing the Cr(VI) level. The other point is that an unspecific reaction of DPC used in spectrophotometry for developing a concentration dependent colour is supposed. This view cannot be confirmed after measuring the absorption maxima of different extracts and metal ions.

4.1. Milacic (9) compared the spectrophotometric method with the AAS method. For the latter it is necessary to extract the Cr(VI) from the phosphate buffer with an organic solvent and to immediately determine the Cr(VI) content. With spectrophotometry higher values were found. The necessity of a second extraction may lead to losses and explains the lower figures. According to the authors diluting the extract to the 5-fold resulted in much higher levels of Cr(VI) determined which was an argument not to employ this method. LGR did the same with Cr(VI) containing extracts and cannot confirm this finding. The point of criticism – the phosphate buffer- was not changed.

4.2. Jambunathan (7) tried to avoid the problems with the IUC-18 determination method caused by coloured leather extracts. The presence of extracted dyestuff together with Cr(VI) makes the exact determination difficult. The correction with a blank is often insufficient. The authors have no alternative for the extraction with a phosphate buffer. For improving the reproducibility of the determination itself they used a flow injection analysis system and for improving the sensitivity a special liquid core waveguide cell. To remove the dye a cation exchange procedure was carried out aimed at the removal of the very limited Cr(III) amount which is perhaps coextracted. After that a bleaching with sodium perchlorate is recommended to destroy the dye. Avoiding the dye by commercially available cartridges was not effective in every case (LGR confirm this finding). Measurement of Cr(VI) was carried out according to the Induction Coupled Plasma – Optical Emission Spectrometry. ICP-OES does measure the whole Cr content therefore it is necessary to cation exchange the extracts prior to the analysis. According to the results ICP-OES seems to be an appropriate method but rather for scientific

questions because the equipment is very expensive and not easy to learn and evaluate. The use of LCW can be recommended only for low levels of Cr(VI) because the results for higher amounts are not reliable.

4.3. In the work of **Font et al.** (3) comparison between the controversially discussed IUC-18 method and determination by capillary electrophoresis was done. A good agreement between the two methods was observed. In discussions the point is the pH of the extraction medium according to the IUC-18 method (7,5-8,0). No change in extraction conditions was made. It should be mentioned that CE is less sensitive than colorimetry and can be applied only for samples with high Cr(VI) contents.

4.3. Another important publication also deals with the determination method of Cr(VI). The research by **Long et al.** (8) was designed to explain the occurrence of Cr(VI) in buffer extracts according to the IUC-18 method as a false positive result. The authors state that Cr(III) is stable in an otherwise uncontaminated phosphate buffer at pH 8 but the pH is high enough for an oxidation of Cr(III).

Findings and conclusions of the authors:

- No Cr(VI) was detected in an acetate buffer at pH 4 when H₂O₂ and Cr(III) were added but it was found in the phosphate buffer at 8. With time the amount was increased. So this buffer oxidised Cr(III). The authors used the H₂O₂ as a surrogate for fatliquors. But the oxidation potential of the derivatives of fatliquors in leather is not known exactly. An oxidation of free Cr(III) with H₂O₂ is possible, of course. In (7) it has been shown that very little Cr(III) is coextracted with the easily soluble Cr(VI) and that cannot result in higher Cr(VI) amounts. A well known fact is that on the other hand the oxidation of Cr(III) does not occur under acidic conditions. A reaction between Cr(III) and fatliquors in leather has been supposed by several authors but either UV light or heating has been necessary for this reaction. A higher pH alone is not enough.
- In both buffer solutions individual leather process chemicals have been reacted with Cr(III). Solutions containing mimosa gave positive results for Cr(VI), only in the phosphate buffer. The same result was observed for the mixture of leather chemicals containing mimosa, too. This is a very unexpected result. Vegetable retanning including mimosa prevents the occurrence of Cr(VI) in leather. LGR found that a much higher offer of mimosa is necessary to obtain this result than of other vegetable tanning agents.
- Adding mimosa to an extract gained from a crust leather retanned with mimosa gave negative results resp. Cr(VI). The explanation given by the authors is that the mimosa retanned leather may contain insufficient leachable Cr(III) so that no reaction is observed. This result shows clearly that there are differences between leather extracts and substances that have already reacted in leather and the solutions not containing other accompanying substances.
- Magnesium chloride was used as an antioxidant according to an EPA method for suppressing Cr(III) oxidation in water samples. The authors showed that Cr(VI) was stable when Mg²⁺ was added to the buffer solutions but the addition reduced the Cr(VI) result of a leather extract by appr. 60%.
- A comparison of employing an artificial perspiration solution at pH 8 with the above mentioned buffer extraction solutions showed varying results.

The work carried out by Long et al. increases the doubts in connection with the IUC-18 method. But the experiments chosen are not able to spread the doubts. It is not correct to do comparison between leather extracts and free substances in buffer solutions. The example of mimosa shows this clearly.

However, the question of extraction medium should be raised. In Germany the phosphate buffer has been chosen because there were previous experiences in connection with the determination of Cr(VI) in water (11). A lot of comparing analytical work for leather between several laboratories has been done.

5. Avoidance of hexavalent chromium in leather

None of the publications gives an absolutely safe “recipe” how to avoid the formation of hexavalent chromium in leather. Results published in the meantime seem to confirm the findings of LGR. For avoiding Cr(VI) it can be recommended: i) not to use natural products such as fish oils ii) to employ vegetable retaining agents iii) to properly adjust pH values in neutralisation and iv) to avoid ammonia as a wetting agent before dyeing and instead, use agents with reducing abilities. A higher moisture content during storage of the leather is positive for lowering or preventing Cr(VI). The positive effect of vegetable retanning agents and the neutral effect of synthetic fatliquors can also be confirmed by the analytical results on leather samples from India carried out at LGR and in which no Cr(VI) was found (15).

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