Comparison of the Inhibition Efficiency of Natural and Synthetic Phenolic Antioxidants on Cr(VI) Formation

by
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Abstract

Gallic acid, gallic acid esters with various chain lengths, tara and tara hydrolysates are compared with one commercially successful synthetic phenolic antioxidant in various protocols for antioxidant testing, and regarding their capability to reduce the proneness to Cr(VI) formation in leather. The results are discussed in light of the Polar Paradox Theory and the possible interaction of the antioxidants with components in the leather matrix. The aim of these investigations is an optimum prevention of Cr(VI) formation in leather.

Introduction

As we ourselves get older with time, our skin becomes wrinkled and our hair gets white, also leather comes into its age. This process occurs with time and largely depends on environmental factors, such as heat or light.

It is a well-established idea that ageing of leather normally starts with a reaction at the fatliquor.[1,2] This is due to the fact that at the a-position to conjugated double bonds of the fatliquor under the influence of heat and light hydrogen radicals are easily abstracted. Auto-oxidation, apart from the constant formation of new radical species leads to the formation of peroxy-radicals and hydroperoxides. Both peroxide species cause a variety of changes in the leather matrix, like bond scissions at the protein chain, partial detanning, formation of aldehydes or ketones or the oxidation of various components. These processes, which may be either radical or electrochemical in nature are complex and are monitored by the different organoleptic, mechanical or purely chemical degradation signs.

The formation of hexavalent chromium, Cr(VI), which can be ascribed as a chemical aging phenomenon, has since more than one decade been in the focus of interest due to a supposed health risk associated with its potential formation.[3] In leather, Cr(VI) originates from the oxidation of free, unbound trivalent chromium, most likely by peroxides or peroxide radicals. Different from other forms of ageing, the amount of Cr(VI) formed under aging conditions is normally reduced simply by increasing humidity. The fact that is largely reversible makes Cr(VI) formation distinct from other aging phenomena.

Antioxidants are generally substances that are used to delay, control or inhibit oxidation. Notably, in leather, for different signs of aging there may be different strategies for choosing the right antioxidant. Regarding the reduction of Cr(VI) an important finding was that the use hydrolysable tannins, such as tara, efficiently suppresses the oxidation of free Cr(III) in leather.[4] Luckily, tara and other hydrolysable tannins were anyway part of the traditionally followed leather making recipes. Hydrolysable tannins contain a high number of H-donating phenol groups, which are known to be very efficient primary antioxidants, reacting predominantly with oxygen cantered radicals. Also other natural compounds containing polyphenolics have been reported to be successful for the suppression of Cr(VI) formation, such as plant extracts of walnut leaves,[5] tannic acid,[6] gallic acid,[7] tocopherol[8] and bayberry extract.[9] As far as synthetic antioxidants are concerned, there is a general recommendation made by Font *et al.*[4] to make use of 1:1 mixtures of phenolic and aminic antioxidants. In fact, fatliquor producers are testing the best synergetic mixture of antioxidants for the very formulation and optimize their incorporation into the final product thus improving the quality and durability of the leather article.

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Manuscript received August 15, 2016, accepted for publication October 26 2016.

Tara contains gallotannins which are basically composed of glucose molecules esterified with gallic acid.[10] Having in mind that the antioxidant moiety in tara is gallic acid, the idea of this work was to compare the antioxidant efficiency of various derivatives of gallic acid with one synthetic phenolic antioxidant. The following antioxidants are compared with each other

- Tara
- Tara hydrolysates (TH)
- Gallic acid
- Alkyl esters of gallic acid with chain lengths from ethyl (C2) to hexadecyl (C16) (GE)
- Fully synthetic phenolic antioxidant (SAOx). A non-yellowing, commercially successful antioxidant was chosen

In hydrolysis of tara, depending on the conditions, both ester bonds between the glucose molecule and gallic acid, as well as depside bonds between gallic acid molecules are split giving gallic acid.[11] Alkly esters of gallic acid are man-made by esterification of the respective alcohols with gallic acid. As antioxidants for leather, neither gallic acid alkyl esters nor tara hydrolysates have been reported so far.

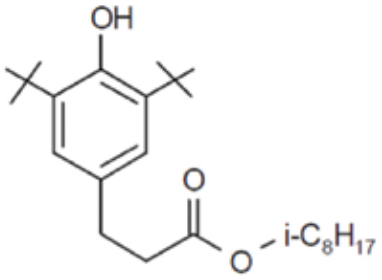
In order to better understand the relation of structure and efficiency, different test protocols used for testing antioxidant efficiency in other areas, like food industry, have been chosen. Finally, the findings have been compared with the efficiency of the components in the prevention of Cr(VI) formation.

Thus, the aim of this work is to compare different derivatives of gallic acid and one commercially successful fully synthetic phenolic antioxidant in various test protocols for antioxidant efficiency, and for their efficiency in supressing the formation of Cr(VI) in leather.

Experimental

Materials

Tara Powder FP of Exandal S.A. (Peru) with a tannin content of 52% and a particle size of <100 mm was used. Anhydrous gallic acid (for synthesis) was purchased from Merck KGaA (Germany). The gallic acid esters were bought from TCI Europe N.V. (Belgium). Fish oil (Aceite pescado bajo I) with an iodine value of 123 gI/100g and an acid value of 13 mgKOH/g was purchased from Industrias Afines S.L. (Spain). The Synthetic Antioxidant (SAOx), Benzenepropanoic acid, 3,5-bis (1,1-dimethyl-ethyl)-4-hydroxy-C7-C9 branched alkyl esters (Irganox 1135), was supplied by BTC Europe GmbH (Germany). The chemical structure of the synthetic antioxidant is as follows:



2,2-Diphenyl-1-picrylhydrazyl (DPPH) 95% was purchased from Alfa Aesar.

All solvents used were of either analytical or spectroscopic grade (Sigma Aldrich).

Methods

Hydrolyzation of tara to 460 g of distilled water 350 g of tara powder and 14 g of concentrated sulfuric acid (95-98%, Acros organics), prediluted 1:10 with water, were added. The suspension was purged with nitrogen at 20°C. Hydrolysis was done at 90°C while stirring for 2, 4 and 8 hours for samples TH1, TH2 and TH3, respectively. After hydrolysis, the samples were cooled down to 60°C and neutralized with NaOH 32% (Merck Millipore) to a pH of 4.0 $\pm$ 0.3.

Total phenolics of tara and tara hydrolysates were determined following the established method[12] using gallic acid as a standard. Absorbance was measured at 755 nm and the results were expressed as gallic acid equivalents (GAE). For the samples of gallic acid esters and the synthetic antioxidant the total phenolic content was calculated based on chemical structure with the following formula:

$$GAE = 170.12\ g\ mol^{-1} * n_{(OH)} / M_w * 3$$

With n(OH) being the number of phenolic OH groups (gallic acid: $n_{(OH)} = 3$) and M_w the molecular weight of the antioxidant (gallic acid: $M_w = 170.12\ g\ mol^{-1}$).

Hydrolysis degree (HD) for the hydrolyzed tara samples was calculated as explained in the work of Chabia *et al.*[11]

For **2,2-Diphenyl-1-picrylhydrazyl (DPPH) scavenging measurements** a simplified set-up to the recommendations by Nenadis [13] was used. In a 25ml flask to 0.0017 g GAE of the test substance (corresponding to 10 mmol GAE), 10ml of 250 mM DPPH solution in ethanol were added, filled up to 25 ml with ethanol, shaken vigorously and left at 20°C in the dark. The decrease in the characteristic absorption of DPPH at 517 nm

after 20 min was measured. The amount of the test substances has been adjusted in order to have a maximum of 90% of radical scavenging activity for the most potent antioxidant.

For **oxidation experiments in fish oil and fish oil emulsions,** amounts of antioxidants corresponding to 0.17 g GAE/ kg fish oil (equivalent to 1 mmol GAE/ kg fish oil) were added to the fish oil or the fish oil emulsion. The samples were kept at 45°C in a shaking machine and the **formation of diene hydroperoxides** was followed by measurement of UV absorbance at 234nm. Prior to the UV measurement, the test samples where diluted to a measurable concentration with hexane or isopropanol for fish oil and fish oil emulsions, respectively. UV determinations were repeated every 2-3 days in order to find the correct conditions of the initial oxidation. The values were corrected by the respective, very small, absorption of the antioxidants themselves.

Results of antioxidant trials in this work are calculated as % inhibition according to

% Inhibition = (C – S)/C* 100,

Where C and S are the test results of the sample without and with antioxidant, respectively. A similar calculation was done for the % of radical scavenging in the DPPH assay.

Leather trial. For the leather trial, a commercially successful sulfited fish oil based fatliquor of 80% concentration having a fish oil content of 50% was used. The different antioxidants were mixed into the fatliquor after being pre-dissolved in a small amount of isopropanol (3% based on amount of fatliquor). The reference consisted of the same fatliquor without any antioxidant, but having the same portion of isopropanol incorporated.

Spanish split wet blue bovine leather was washed (60 min, 0.2% formic acid, 1% ethoxylated fatty alcohol), re-chromed (4% Cr-Sulfate 33% Basicity, 1% alumn. silicate), neutralized (2% Na-formate, 2% Na-bicarbonate, 110 min) to pH 6.5 and then fatliquored with 2x7% of aforementioned fatliquor at 50°C for 2x45 min. After that, the fatliquor was fixed with 3 additions of 1% of formic acid to a bath pH of 3.7. The leathers were horsed-up air dried horizontally. All % are based on shaved weight.

Cr(VI) measurement in leather were conducted following DIN ISO 17075:2008-02, after a pre-ageing of 24h at 80°C with air flow and with a repose time of 1h. The leathers were cut to pieces of approximately 4x4mm before aging.

Heat yellowing was done for 144h at 100°C with air flow, followed by the determination of yellowness index according to ASTM E313.

Results and Discussion

Hydrolysis of tara samples. The tara used for hydrolysis was found to have an amount of free phenolics of 49 ± 2 g GAE/100g, what coincides with literature data.[14]

The following values were found for the hydrolysis degree (% HD) and amount of free phenolic content (calculated on 100% active matter) for the three samples investigated (Table I).

Table I
Results for hydrolysis degree (%HD) and Free phenolics for hydrolyzed Tara samples.

	TH1	TH2	TH3
% HD	21 ± 2	38 ± 3	75 ± 5
Total Phenolics, g GAE/100g	44 ± 4	37 ± 4	38 ± 4

These data are in accordance with the values found by Chambia.[11] The amount of free phenolics only drops slightly by hydrolysis, what is attributed to the hydrolysis of the depside bonds between gallic acid molecules.[10] The hydrolysis of the bonds between gallic acid and the sugar molecule does not lead to an increase in free phenolic content, since the OH-groups of gallic acid are not involved.

The trials with antioxidants were done based on the same **total phenolic content** (expressed as GAE) and not on the same amount. Having in mind that phenolic moieties are scavenging free radicals, this molar approach gives a more correct understanding of the structure – efficiency correlation of the respective molecules. The GAE values used are depicted in Table II.

DPPH radical scavenging. The scavenging of DPPH radicals is an easy tool for assessing the efficiency of an antioxidant in a very simple matrix. The results for DPPH radical scavenging are depicted in Figure 1. Surprisingly, the efficiency of all gallic acid derivatives is high as compared with the synthetic antioxidant, giving a generally promising picture for the performance of this antioxidant group. It is known that in the DPPH assay, one molecule of alkyl gallate, regardless of its alkyl chain length, can be oxidized three times by DPPH radicals into the corresponding quinone.[15] For Tara, there will be a similar situation, what explains that gallic acid, tara and the gallic acid alkyl esters were all in the same range. This, for the gallic acid esters coincides with the results of Maldonado.[16] For the tara hydrolysates, the presence of salts remaining after neutralization is surely effecting the result.

Table II
Values of gallic acid equivalents (GAE) of the samples tested.

Component	GAE
Gallic acid	1.00
GE C2	0.86
GE C4	0.75
GE C8	0.60
GE C12	0.50
GE C16	0.40
Tara	0.49
TH1	0.14
TH2	0.13
TH3	0.13
SAOx	0.15

Measurement of diene hydroperoxides. Diene hydroperoxides are structures, which are formed in the very beginning of the oxidation of the fat. The formation of these species can be followed by changes in the UV-absorption at 234 nm, after an appropriate dilution. All trials have been repeated 3 times in order to assure more reliable data.

With the idea to test the efficiency of the antioxidants for fatliquor protection, trials with both fish oil and with anionic fish oil emulsions have been done. Fish oil has been chosen as test substrate since it shows, due to the high number of reactive double bonds, a high proneness to oxidation and is thus often discussed in the context of Cr(VI) formation in leather.[1,4]

In the diene hydroperoxide measurement for **fish oil** it is clearly seen that the efficiency of the gallic acid esters is very high, with a maximum efficiency at the octyl gallate. From the polar paradox theory,[17] which indicates that the antioxidant efficiency of polar antioxidants is better in non-polar media and vice versa one would assume a better behavior with shorter hydrophobic chains. The polar paradox takes into account the importance of surface phenomena in the oxidation process: polar substances, which are not soluble in the bulk oil, tend to be found at the oil-air or oil-water interface, where the very oxidation takes place. In emulsions, on the other hand, non-polar antioxidants are favored since they are dissolved in the small oil droplets, at the surface of which the very oxidation is happening. When amphiphilic antioxidants, like in this case gallic acid esters are used, it is not unusual that a parabolic behavior of the antioxidant efficiency in function of the alkyl chain length is observed.[18,19]

A possible explanation for this parabolic behavior is the surface activity of the molecule. The surface activity of alkyl gallates measured by the reduction of surface tension was found to have a maximum at a carbon chain length of C8.[15] At longer chains the hydrophobic nature of the alkyl chain predominates and the respective alkyl gallates are no longer water-soluble. So, in the C-chain dependence of the efficiency there are two components: increasing surfactant properties making the alkyl gallates more likely to form micelle-like structures around the small air-bubbles in the fish oil (C2→C8), and increasing tendency for them to be dissolved in the bulk oil (C8→C16).

The efficiency of the structure-wise very different synthetic antioxidant in the inhibition of fish oil oxidation was found to be slightly less than for the gallic acid esters, what can be explained in term of a higher lipophilicity.

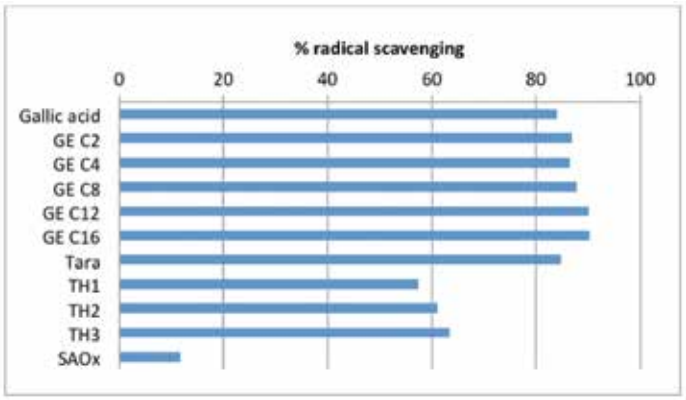


Figure 1. Percent radical scavenging for DPPH scavenging assay.

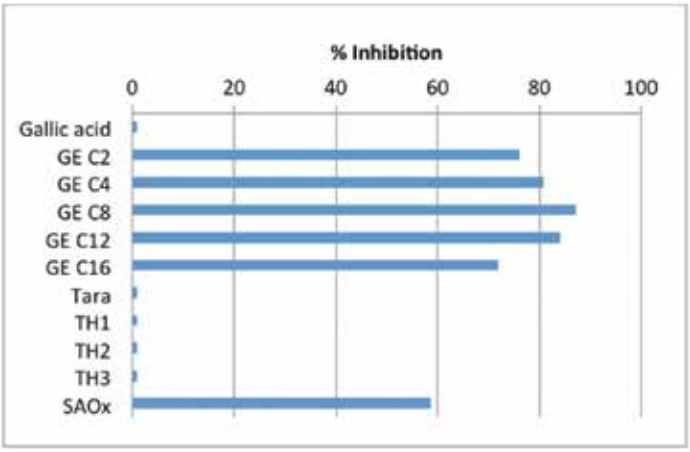


Figure 2. Effect of antioxidants on the oxidation of fish oil, formation of diene hydroperoxides after 7 days.

Regarding gallic acid, tara and tara hydrolysates, the solubility of these components is too low: these substances precipitate and cannot be hold in suspension during the long duration of analysis (Figure 2).

For testing the antioxidant efficiency in emulsions, various emulsions have been preliminarily tested. In sulfited or sulfated fish oils, the formation of diene hydroperoxides cannot be followed due to an already high absorption at 234 nm, which is surely due to the fact that in the respective chemicals reactions conjugated structures are already formed. Thus, a system with anionic emulsifiers added to the fish oil has been chosen. The emulsion tested had the following composition:

- 22% Fish oil
- 9% Oleic acid, Na salt
- 7% Fatty alcohol C1214 Sulfate, Na salt
- 62% water

This emulsion was found to be stable over the entire test period, what is a necessary prerequisite for antioxidant testing in emulsion. As depicted in Figure 3, in this case all antioxidants do show some inhibition on oxidation, surely due to a generally good incorporation by the presence of an emulsifier. The best results are obtained for tara hydrolysates with higher hydrolysis degree, followed by tara, what can probably be explained in terms of a better solubility of the hydrolysates in comparison with tara itself. The gallic acid esters do again show a parabolic behavior, with a minimum at dodecyl gallate. The polar paradox would in this case predict a higher efficiency for longer chain lengths, since the solubility in the very oil, the oxidizing substrate, is increased. In other works it has also been found that the effect of the alkyl chain lengths depends largely on the emulsifier system used and does generally not follow the polar paradox.[20] An interesting finding in this respect is the very good behavior of all gallic acid based antioxidants in the prevention of oxidation in the emulsion. In fact, the majority of them is more efficient than the synthetic antioxidant, implying that for the oxidative protection of the very fatliquor, gallic acid based antioxidants are a fully valid alternative.

Assessment of reduction of Cr(VI) formation in leather. In the leather trials, which for the sake of reliability were repeated, care was taken in order to have a homogeneous distribution of fat in the leather. Notably, in preliminary trials it was found that reproducibility is best when split wet blue is used, and the final drying of the leathers is done horizontally, rather than by hanging the leathers. This surely avoids possible migrations during drying. The results given (Figure 4) are based on average values of samples taken from different areas of the respective leathers.

When an amount of 30mmol GAE antioxidant /kg of fatliquor was used, what would correspond to 0.5% GAE, the inhibition brought about by alkyl gallates with long carbon chain is far above 90% and thus is as high as with the synthetic antioxidant. In fact, with the increasing lipophilic character of the alkyl gallates they have a higher tendency to be dissolved in the oil droplets of the emulsion. When the leather is dried, the alkyl gallates are deposited together with the oil. Notably, due to the fact that mobility of the components in dry leather is very limited, it is of foremost importance that the antioxidant is evenly distributed on the very oil and does not form clusters or is associated in other parts of the leather. Thus, as a general principle, the polar paradox seems to fully apply for prevention of Cr(VI) in leather, taking into account that the fatliquoring is done in a polar environment, and thus non-polar antioxidants have a higher efficiency.

The synthetic antioxidant is a tailor-made molecule with an enhanced solubility in oil, what, according to the polar paradox makes it very suitable for use in emulsions. When the emulsion

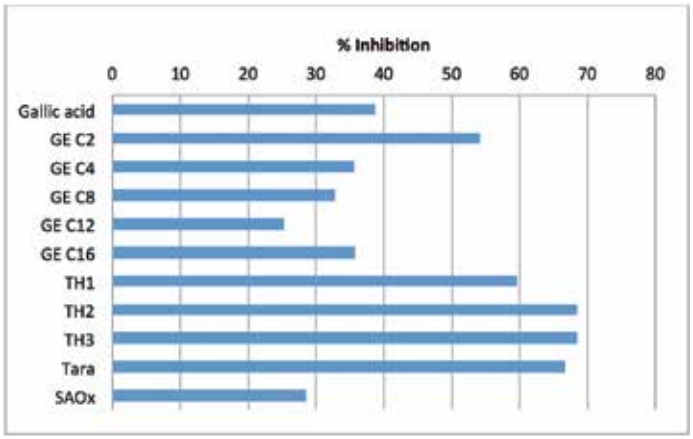


Figure 3. Effect of antioxidants on the oxidation of fish oil emulsions; formation of diene hydroperoxides after 3 days.

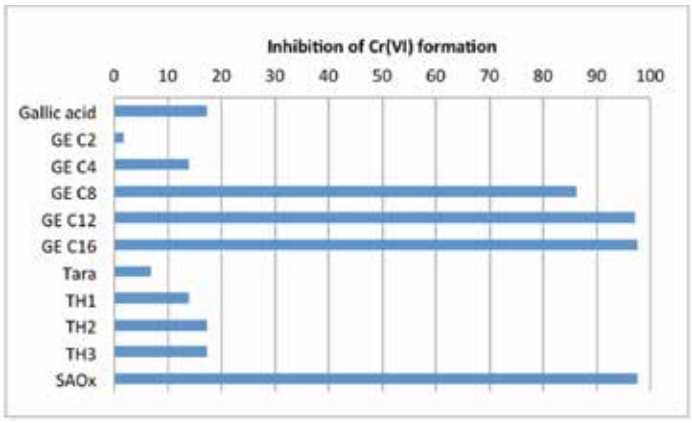


Figure 4. Results of inhibition of Cr(VI) formation using 0.5% GAE antioxidant based on fatliquor weight.

dries out, the antioxidant which is dissolved inside of the oil droplets will be again be located very close to the tiny oil drops. Regarding general reactivity it has to be mentioned that the bulky substituent in o- and p-position to the phenol group increases its reactivity reducing the O-H bond dissociation enthalpy.

It can also be seen that the protective efficiency of gallic acid, based on the same phenolic content, is slightly better than of tara. On the other hand, when tara is hydrolyzed, activity increases and finally reaches the level of gallic acid. In the case of tara a drawback is probably its limited solubility, which is increased when tara is hydrolyzed.

Surprisingly, gallic acid shows a higher efficiency in suppressing Cr(VI) formation than ethyl and butyl gallate. Gallic acid and it salts are very hydrophilic and should therefore be preferably located in the aqueous phase of the emulsion rather than the oil drops. In this case, however, there may be another effect, associated with the anionic moiety. In leather, both the anionic sulfited fish oil and the anionic gallic acid salt are, during fatliquor fixation, bound to the cationized aminic groups, what would bring them in proximity to one and each other.

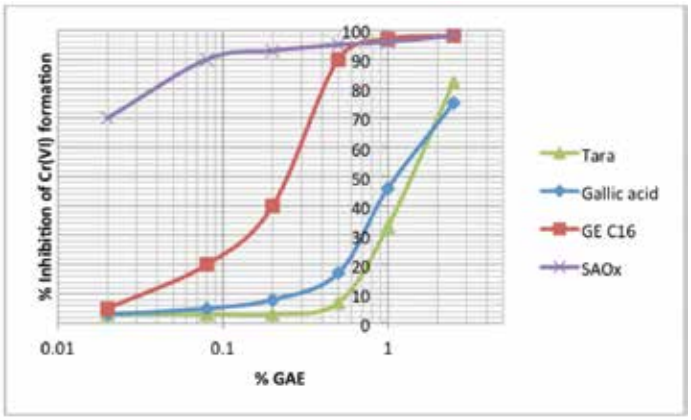


Figure 5. Results of inhibition of Cr(VI) with different concentration of Antioxidants.

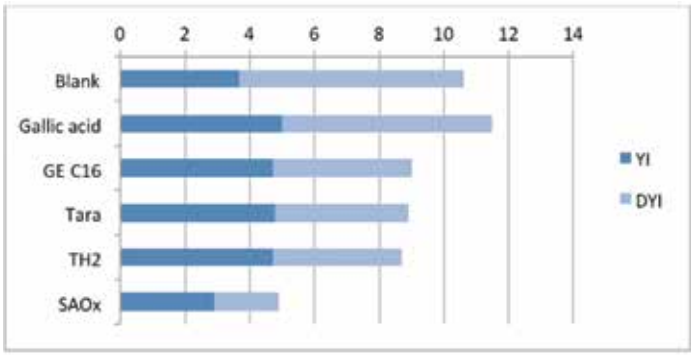


Figure 6. Yellowness index (YI) of crust and heat yellowing 144h at 100°C expressed as difference in YI (DYI). Use of 0.5% GAE.

The concentration-efficiency dependence of four selected antioxidants is depicted in Figure 5. It is clearly seen that the synthetic antioxidant has a very high efficiency at lower concentration. Hexadecyl gallate is in-between gallic acid and tara. The latter two give similar results, gallic acid performing somewhat better than tara. It has to be taken into account that the trial was done based on the same phenolic content, if the same weight would be used, one would find an even larger difference in favor of gallic acid.

Furthermore, **general leather properties** have been assessed, at a standard concentration of 0.5% of GAE. It was found that the synthetic antioxidant does practically not change leather properties. It gives a cleaner crust and significantly less yellowing in the course of thermal treatment. With tara, the leather becomes harder and fuller, something what is reduced substantially, when hydrolyzed tara is used. As far as yellowing is concerned, tara, tara hydrolysates and gallic acid esters behave similarly, giving a slight reduction in thermally induced yellowing. With gallic acid, there is a significant yellowing in crust and especially after thermal aging (Figure 6).

Conclusion

In simulation trials it was found that, depending on the test protocol used, gallic acid based antioxidants gave very good results, which were often better than the results obtained with the synthetic antioxidant chosen for comparison. In leather, long-chain gallic acid esters gave a very good protection against Cr(VI) formation. The synthetic antioxidant was superior especially at low usage amount. Due to the low mobility of the antioxidants in dry crust leather it is very likely that a localization of the antioxidant on the surface of the oil after drying is of foremost importance. This gives a clear advantage to very non-polar, oil soluble antioxidants. Antioxidants with high surface activity or anionic moiety may also be beneficial, a fact that should be studied more in detail.

For making leathers that do not tend to form Cr(VI) the following points are of significant importance:

- Minimizing amount of unbound Cr(III)
- Moderate neutralization
- Use of securely protected fatliquors

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