

Natural phenolics preventing aging in leather

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Abstract

Gallic acid esters are a class of polyphenolics that have been found in our previous work to be very suitable antioxidants for leather securely preventing the formation of Cr(VI). In fact, alkyl gallates with long carbon chain have an efficiency that is far superior to tara or gallic acid. In this work we compare gallic acid derivatives with DL-tocopherol (Vitamin E) and tocopherol derivatives, discussing the results in antioxidant efficiency in leather in the framework of the polar paradox and the efficiency of the very phenolic groups. The final aim of this work is the improvement of sustainability of leather by increasing quality and durability of leather articles and a better protection against the formation of Cr(VI) by natural ingredients.

Keywords: antioxidants, Cr(VI), tocopherol, gallic acid esters

1. Introduction

Leather is a high quality material, which, for considerations of sustainability should preserve its natural beauty for many years. Very good mechanical and chemical fastness and its durability make leather a material which is used for much longer time than synthetic alternatives. However, there are aging processes occurring in the leather deteriorating its quality. Normally, the extent of leather aging depends on environmental factors, such as heat or light. Its mechanism has been studied in detail and it is a generally accepted fact that aging of leather starts with a reaction at the fatliquor. The initial step of this process is that a hydrogen radical is abstracted at the α -position to a conjugated double bond of the fatliquor (Candar et al. 2001; Segura et al. 2000) forming a carbon centered radical.

Followed by this initiation step, more radicals including oxygen centered peroxy radicals are formed in a cascade type reaction. As a result, many unwanted deterioration processes are occurring in the leather matrix, at the collagen and at many other components present in the leather. The entire aging process is thus a chain-reaction, called autoxidation, which can be divided in initiation, propagation and termination.

The result of the autoxidation is distinguished by different phenomena by which the extent of aging can be quantified: they can be divided into organoleptic, mechanical or purely chemical degradation signs.

There are basically two possibilities to make leather more durable. One can

(a) Prevent the radical formation (initiation). Although difficult, by optimizing the storage conditions of leather or by using suitable UV blocking finishing or special UV absorbers, aging processes can be significantly slowed down.

(b) Introduce substances, which terminate the chain reaction without creating new radicals. These substances, called primary anti-oxidants, normally react with the oxygen centered peroxy-radicals formed during autoxidation and which, due to their high reactivity, are of foremost importance for the degradation of leather

The antioxidants use for the protection of leather are basically of three different groups

- Phenolic compounds
- Aromatic amines
- Hindered amines

There are different approaches for using antioxidants. Often, antioxidants are part of the fatliquor composition, what is very reasonable, since their deposition in close vicinity to the

fatliquor molecules guarantees a high probability that they show an optimum effect. On the other hand, many vegetable and some synthetic type tanning agents are themselves acting as phenolic type antioxidants. Thus, a proper retannage can give a substantial protection against at least some signs of aging. As far as natural antioxidants in leather are concerned, studies with hydrolysable tannins, especially tara, for preventing Cr(VI) formation have been done (Font et al. 1999). Hydrolysable tannins contain a high number of H-donating phenol groups, which are known to be very efficient primary antioxidants. Also other natural compounds containing polyphenolics have been found successful for the suppression of Cr(VI) formation, such as plant extracts of walnut leaves (Bayramoglu et al. 2012), tannic acid (Colak et al. 2014), gallic acid (Devikavathi et al. 2014), tocopherol (Liu and Latona 2003) and bayberry extract (Ma et al. 2012). Our recent work was focused on the antioxidant activity of gallic acid esters and tara hydrolysates (Kilikli et al. in print). As far as synthetic antioxidants are concerned, there is a general recommendation made by Font et al. (1999) to make use of 1:1 mixtures of phenolic and aminic antioxidants. In fact, fatliquor producers are testing the best synergetic mixtures of antioxidants for the very formulation and optimize their incorporation into the final product thus improving the quality and durability of the leather articles their products are used for. In the current paper we would like to compare different natural antioxidants regarding their efficiency in various aging protocols.

The following antioxidants are compared with each other

- Gallic acid
- Hexadecyl gallate (C16 Gallate)
- fully synthetic phenolic antioxidant (SAOx). A non-yellowing, commercially successful antioxidant was chosen
- DL-tocopherol (Vitamin E)
- DL-tocopheryl acetate (Vitamin E acetate)
- Trolox

Notably, the aim is to investigate the structure-efficiency relation of the different compounds. For this reason, the comparison was done based on the same concentration of phenolic OH-groups rather than the same amount.

2. Materials and methods

Anhydrous gallic acid (for synthesis) was purchased from Merck KGaA (Germany). Hexadecyl gallate was bought from TCI Europe N.V. (Belgium). Tara Powder FP of Exandal S.A. (Peru) with a tannin content of 52% and a particle size of <100 µm was used. DL-Tocopherol (Vitamin E) was purchased from Klüver & Schulz (Germany), Trolox 96% from Acros Organics (Belgium), DL-Tocopheryl Acetate 97% (Vitamine E Acetate Care) was supplied by BASF (Germany). 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). All solvents used were of either analytical or spectroscopic grade (Sigma Aldrich).

Total phenolics of tara was determined following the established method (Chambia et al 2013) using gallic acid as a standard. Absorbance was measured at 755 nm and the result was expressed as gallic acid equivalents (GAE). For all other antioxidants the total phenolic content was calculated based on chemical structure with the following formula:

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

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

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% Alum 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 horse-drawn 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 a repose time of 1h. The leathers were cut to pieces of approximately 4x4mm before aging. Inhibition was calculated as

$$(2) \text{ % Inhibition} = (C - S)/C^* 100,$$

where C and S are the test results of the sample without and with antioxidant, respectively.

Shrinkage temperature T_s was measured in a mixture of glycerin:water 1:1 following DIN EN ISO 3380. For the assessment of aging, the decrease in shrinkage temperature by a thermal treatment for 24h at 80°C was determined. Leathers used for the assessment of shrinkage temperature contained 0.2% GAE of antioxidants.

Odor was measured after 2h at 80°C using leather samples containing 0.2% GAE of antioxidant. The evaluation of rancid type odor

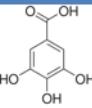
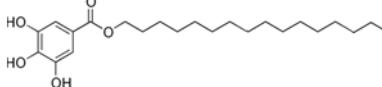
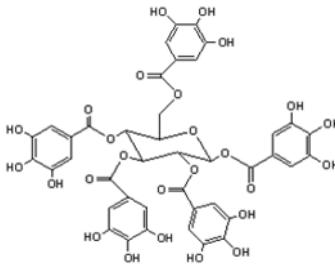
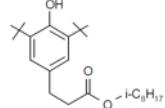
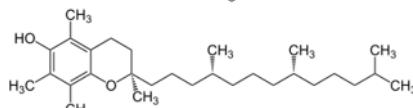
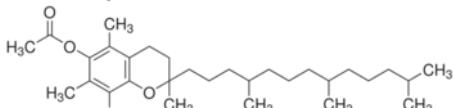
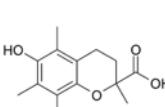
was done by 4 experienced lab technicians and expressed as scores from 1 (very noticeable) to 5 (not noticeable).

Heat yellowing was done for 288h at 100°C with air flow, followed by the determination of yellowness index according to ASTM E313. The leather used for heat yellowing contained 0.1 % GAE of antioxidant. Results are expressed as difference in Yellowness Index, ΔYI

3. Results and discussion

As already explained, the trials with antioxidants were done based on the same **total phenolic content** (expressed as gallic acid equivalents, GAE) and not based on the same amount. Having in mind that it is the phenolic moieties that are scavenging free radicals, this molar approach gives a better understanding for the efficiency of the very molecule. The GAE values and the chemical structure of the antioxidants used are depicted below:

Table 1. Values of gallic acid equivalents (GAE) and chemical structure of the samples tested

Component	GAE	Chemical Structure
Gallic acid	1.00	
Hexadecyl Gallate	0.40	
Tara	0.49	
SAOx	0.15	
DL-Tocopherol	0.13	
DL-Tocopheryl acetate	(0.12)	
Trolox	0.23	

Results

Assessment of reduction of Cr(VI) formation in leather. In many of our previous trials with antioxidants we had found that the measurement of proneness to Cr(VI) formation, a chemical sign of aging, is in fact a very precise means to determine the capability of an antioxidant to prevent aging since very exact and reproducible values are obtained. The results given are based on average values of samples taken from different areas of the respective leathers.

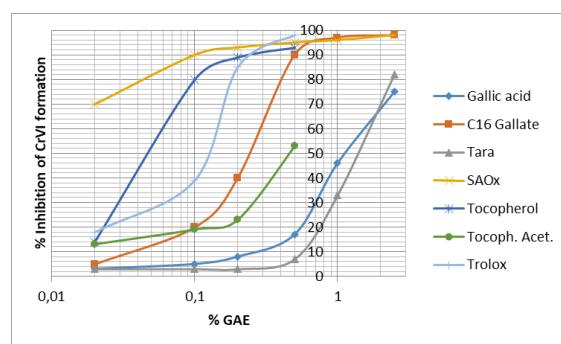


Fig. 1. Results of inhibition of Cr(VI) formation

Measurement of decrease shrinkage temperature.

The decrease of shrinkage temperature, a physical sign of leather aging, by thermal treatment can be attributed to a partial rupture of chemical bonds in the collagen or between collagen and the tanning agent, possibly by direct attack of oxygen centered peroxide radicals. Thus, the evaluation of the effect an antioxidant has on the decrease of shrinkage temperature is another means for the determination of the efficiency of an antioxidant. Results obtained with 0.2% GAE of antioxidants are depicted below

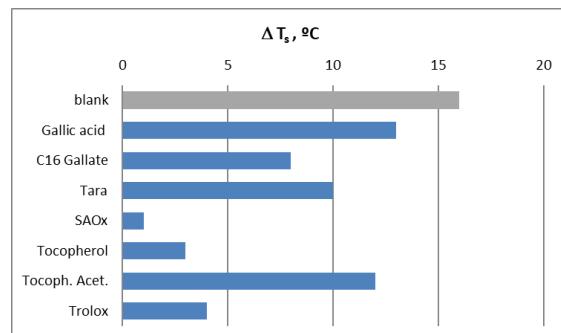


Fig. 2. Decrease in shrinkage temperature in relation to the different antioxidants used

A possible evolution of rancid odors by oxidation processes is of importance for the quality and usage time of a leather article. These odors originate from the formation of aldehydes and ketones, often stemming from the reduction of peroxides of the fatliquor, natural grease or other components of the leather matrix.

Results for the assessment of odor with the use of 0.2% GAE of the different antioxidants are displayed below.

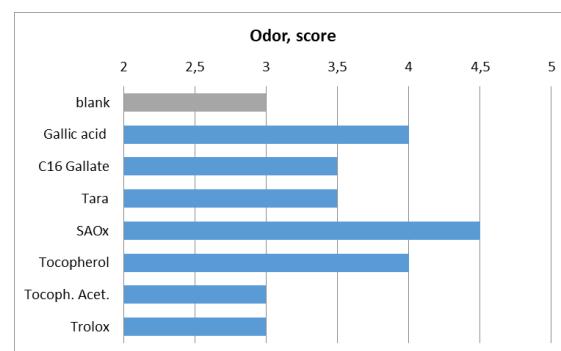


Fig. 3. Odor formation with the use of different antioxidants

Heat Yellowing is the probably most prominent method for assessing aging in leather. Generally, yellowing is due to the formation of chromophoric groups, especially conjugated double bonds, in the course of autoxidation. When investigating different antioxidants, the interpretation on the basis of heat yellowing values is at times misleading, since some very powerful antioxidants yellow themselves, give an intrinsic coloration to the leather or interact with other components in the leather matrix. The trials presented here were done with 0.1% GAE of antioxidant: a relatively small quantity has been chosen in order to keep the yellowing of the antioxidant itself low.

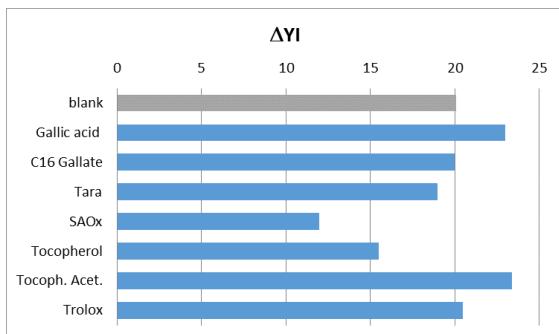


Fig. 4. Heat yellowing by the use of different antioxidants

Discussion

When used based on the same phenolic content, the efficiency of tara and gallic acid for the suppression of Cr(VI) formation are similar. As had been demonstrated in our previous work, long chain alkyl gallates are very efficient antioxidants for leather fatliquors. 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 dries, 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. The general empirical principle, which is behind this explanation is called the polar paradox, which predicts that the efficiency of a non-polar antioxidant is better in a polar medium and vice versa (see Laguerre et al. 2015). A polar antioxidant would have a high affinity to the aqueous phase, which of course does not oxidize at all. Notably, a polar antioxidant works very well for a bulk oil, since it is situated at the interface of the oil and tiny air bubbles inside of the oil, where the very oxidation is taking place.

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 therefore non-polar antioxidants have a higher efficiency.

In the other aging phenomena investigated in this paper, the behavior is more complex. Gallic acid gives rise to a relatively strong yellowing, tara and hexadecyl gallate yellow less. On the other hand, for the prevention of rancid odors, gallic acid was found to perform slightly better than tara or hexadecyl gallate. As far as the decrease in shrinkage temperature is concerned, the long chain alkyl gallate performs better than tara or gallic acid. There might be, however, an interaction of the polyphenolics with the collagen, competing with the influence of the substance as antioxidant.

Regarding the Vitamin E derivatives, their efficiency in suppressing Cr(VI) formation when calculated on the same phenol content is in general significantly superior to gallic acid derivatives. This can be explained by the methyl substituents adjacent to the phenolic OH-group which decrease the electron density in the phenolic ring thus making the abstraction of the phenolic H-radical energetically favorable. In fact, Vitamin E is known to be one of the most powerful natural antioxidants. Trolox had been developed as a water soluble analog of Vitamin E. Again, as the polar paradox would predict, the higher polarity is a disadvantage when used in emulsions. Having a carboxylic group it is also possible that trolox binds to the cationic centers in the collagen and thus actually competes with the fatliquor. With gallic acid esters it had been found, though, that this can also be of some advantage. Notably, the Cr(VI) suppressing efficiency of gallic acid had been found to be better than of ethyl gallate, although from point of view of the polar paradox it would be vice versa. A possible explanation is that the amount of antioxidant actually present in the leather is increased by ion-ion interactions at the anionic moiety. The finding with Vitamin E acetate, on the other hand, is a little confusing. This antioxidant is normally used for applications in living organisms, where the ester bond is enzymatically hydrolyzed leaving the phenolic group open. The Vitamin E acetate used contains only up to 1% of free tocopherol, so

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this would not explain its considerable efficiency in Cr(VI) suppression. One possible explanation might be that in the conditions of leather treatment, supposedly by acid catalysis during fixation, some of the ester bonds may break up giving free Vitamin E. It would also be possible that it is the reductive action rather than the radical scavenging activity, which gives lower Cr(VI) values with Vitamin E acetate.

In the other tests for aging, it turned out that Vitamin E does always perform better than trolox, what would be in line with the findings and explanation given above. For Vitamin E acetate, on the other hand, very little until no protection against other signs of aging has been found. This altogether would give rise to the conclusion that Vitamin E acetate does not form free Vitamin E during leather processing and that the effect which had been found in Cr(VI) suppression could be attributed to electrochemical reduction rather than radical scavenging.

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 dries out, the antioxidant which is dissolved inside of the oil droplets will be deposited in vicinity to the tiny oil drops.

Regarding general reactivity it has to be mentioned that the bulky alkyl substituents in o- and p-position to the phenol group increases drastically its reactivity reducing the O-H bond dissociation enthalpy.

4. Conclusion

In Cr(VI) suppression, Vitamin E and trolox perform generally better than gallic acid derivatives, surely due to the effect of the methyl substitution reducing the electron density at the phenolic ring. For both gallic acid and tocopherol derivatives the finding would be that protection increases with the decrease in polarity of the molecule, something that can be explained in terms of the polar paradox, the antioxidants being used in emulsions. Notably, the polar paradox paradigm has a special importance in leather, due to the practical immobility of the components under the conditions of aging of dry leather. In the investigation of the other aging phenomena the processes occurring are more complex and only partially understood. Vitamin E and trolox give a lower decrease in shrinkage temperature. In yellowing, the very strong yellowing of gallic acid is seen as a disadvantage. The highly oil-soluble, non-polar synthetic antioxidant used for comparison has an excellent efficiency in all aging protocols investigated.

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