(REFEREED RESEARCH)

ANTIOXIDANT EFFECT OF TANNIC ACID ON FORMATION OF FORMALDEHYDE AND HEXAVALENT CHROMIUM COMPOUNDS IN LEATHER

TANNİK ASİDİN DERİDE SERBEST FORMALDEHİT VE ALTI DEĞERLİKLİ KROM BİLEŞİKLERİNİN OLUŞUMUNUN ÜZERİNE ANTİOKSİDAN ETKİSİ

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ABSTRACT

The presence of formaldehyde and hexavalent chromium in leather products, results from the inclusion of formaldehyde in chemical manufacturing process of industrial chemicals, and the oxidation of Cr (III), which is used as tanning agent in leather tanning industry, to Cr (VI) under certain conditions. In this study, wet-blue sheep skins were treated with different concentrations of tannic acid such as 0.1, 0.5, 1, 2 and 3% at retanning process in order to investigate the antioxidant effect of tannic acid on chromium (VI) and free formaldehyde formation in leather. For this purpose following the retanning process, formaldehyde content of leathers were analyzed according to ISO TS 17226 method with HPLC device. Hexavalent chromium formation was forced by exposing leather samples to accelerated ageing conditions, such as high temperature and UV. The chromium (VI) content on leather samples were determined in accordance with TS EN ISO 17075 standard procedure. The physical properties of final leathers were also investigated. Inhibitory efficiency of tannic acid both on hexavalent chromium and formaldehyde was attained at concentrations above 1% tannic acid. The offer of 3% tannic acid fulfilled the Eco-label criteria for footwear and provided lower chromium (VI) values than 3 ppm. Besides, all four tested concentrations of tannic acid maintained the formaldehyde concentrations under restricted limits. The improvement effect on the physical characteristics of leathers was observed in direct proportion of increasing tannic acid concentrations. The results indicated that tannic acid has a remarkable antioxidant effect on chromium (VI) and free formaldehyde formation in leather.

Key Words: Cr (VI), Formaldehyde, Accelerated ageing, Tannic acid, Leather.

ÖZET

Deri ürünlerinde serbest formaldehit ve altı değerlikli krom bileşiklerinin varlığı, formaldehitin endüstriyel kimyasalların üretim proseslerinde kullanılması ve deri endüstrisinde tabaklama maddesi olarak kullanılan krom (III)'ün belirli koşullar altında krom (VI)'ya okside olmasından kaynaklanmaktadır. Bu çalışmada kromla tabaklanmış deriler retenaj işleminde 0,1, 0,5, 1, 2 ve %3 oranlarında tannik asit ile muamele edilerek, tannik asidin antioksidan etkisinin altı değerlikli krom ve serbest formaldehit oluşumu üzerine etkisi araştırılmıştır. Bu amaçla retenaj işlemi sonrasında derilerin serbest formaldehit içerikleri ISO TS 17226 metoduna göre HPLC cihazı kullanılarak analiz edilmiştir. Deri örnekleri yüksek sıcaklık ve UV gibi hızlandırılmış yaşlandırma koşullarına maruz bırakılarak derilerde altı değerlikli krom oluşumu sağlanmıştır. Deri örneklerindeki krom (VI) miktarları TS EN ISO 17075 standardına göre belirlenmiştir. Mamul derilerin fiziksel özellikleri üzerine olan etkisi de incelenmiştir. Tannik asidin altı değerlikli krom ve formaldehit oluşumu üzerine engelleyici etkisi, %1 tannik asit konsantrasyonunun üzerindeki değerlerde gözlenmiştir. %3 tannik asit kullanımı ile krom (VI) değerleri 3 ppm'in altında elde edilmiş ve ayakkabı için eko etiket kriterlerini sağlamıştır. Bunun yanında uygulanan tüm tannik asit konsantrasyonları formaldehit miktarını kısıtlanan limit değerlerinin altında elde edilmesini sağlamıştır. Tannik asidin artan konsantrasyonları mamul derilerin fiziksel özellikleri üzerine olumlu bir etki göstermiştir. Çalışmadan elde edilen sonuçlar tannik asidin derideki krom (VI) ve serbest formaldehit oluşumu üzerine etkin bir antioksidan etkisinin olduğunu göstermektedir.

Anahtar Kelimeler: Cr (VI), Formaldehit, Hızlandırılmış yaşlandırma, Tannik asit, Deri.

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1. INTRODUCTION

Strict regulatory measures taken in recent years triggered manufacturers to design their products to have lower ecological, toxicological risks on environment and public health. In this context, chemical substances are compiled into lists following the regulations such as European Union Registration Evaluation Authorization and Restriction of Chemicals (REACH) and Restricted Substance List (RSL) by considering their potential hazardous risks to human health or environment, and specific regulatory or restriction actions are taken by governmental and international environmental protection agencies.

Restricted substance lists have a large variety of chemical substances and only a few of the listed substances are relevant to leather. Formaldehyde and hexavalent chromium compounds are considered within the restricted substance lists and are of real concern for leather and their amount in the consumer leather article is restricted (1). In the European Union restricted limits of free formaldehyde content in leather may vary from 20 ppm for baby shoes up to 100 ppm when the leather is in contact with the skin, 150 ppm for shoe uppers and 400 ppm for leather without permanent contact with the skin (2,3). The European Eco-label for footwear criteria 2009/563/EC specified allowable level of formaldehyde as 150 ppm. And accordingly, it is obligatory to provide chromium (VI) contents lower than 3 ppm to obtain the accreditation for the use of the European eco-label for footwear.

The presence of formaldehyde in leather products, results from their inclusion in manufacturing process of industrial chemicals used in leather production. They are used predominantly as a chemical intermediate in the synthesis of some syntans, such as melamine formaldehyde resin, and free formaldehyde may be released under certain conditions, due to the reversible reactions. On the other hand hexavalent chromium compounds are not directly used in leather production, however Cr (III) compounds, which are the most widely used tanning agent in leather tanning industry, have the risk to be oxidized to Cr (VI), which is both acutely and chronically toxic (4) due to use of unsaturated fatty acid containing fatliquoring agents, and exposure to environmental factors such as ultraviolet light, heat and high neutralization and dyeing pH (5-7).

The exposure to formaldehyde and hexavalent chromium occurs predominantly as a result of inhalation or dermal contact, which pose a serious hazardous impact on human health such as respiration problems, skin irritation, genetic deformation and high levels of exposure has been linked to some types of cancers (8,9). Therefore it is important to reduce or eliminate formation of both compounds in leather products (10-12).

The antioxidant and inhibitory effects of various polyphenols on formation of formaldehyde and hexavalent chromium in leather production has been studied previously (13-15). The antioxidant activity (16) of tannic acid, which is a commercial form of hydrolysable tannin and a water-soluble polyphenol, was investigated by applying in different stages of leather production such as soaking (17) and pickling (18), however limited published data is available on the effect of tannic acid on chromium (VI) formation in leather production (19).

In this work, the influence of tannic acid application in retanning process on chromium (VI) and free formaldehyde formation in leather by making use of its radical scavenging and antioxidant feature was studied. Leather samples treated with tannic acid were exposed to different artificial ageing conditions prior to Cr (VI) determination, to identify the most important variables affecting this weathering process and to check for interactions. Also, the effect of tannic acid on physical features of the leather was investigated.

2. MATERIAL AND METHOD

2.1 Material

Dry-salted metis origin sheep skins were used for the retanning experiments. Commercial grade conventional process chemicals used for leather processing. Tannic acid and the chemicals used for the analysis were of analytical reagent grade and purchased from Merck.

2.2 Retanning procedure

Six dry-salted sheep skins were processed conventionally, using a standardized formulation until the retanning process. Following the neutralization to pH 5.5, skins were cut into pieces of 30x30 cm each, and separated into six groups. Five groups were retanned with the offer of 0.1, 0.5, 1, 2 and 3% tannic acid in accordance with the formulation presented in Figure 1.

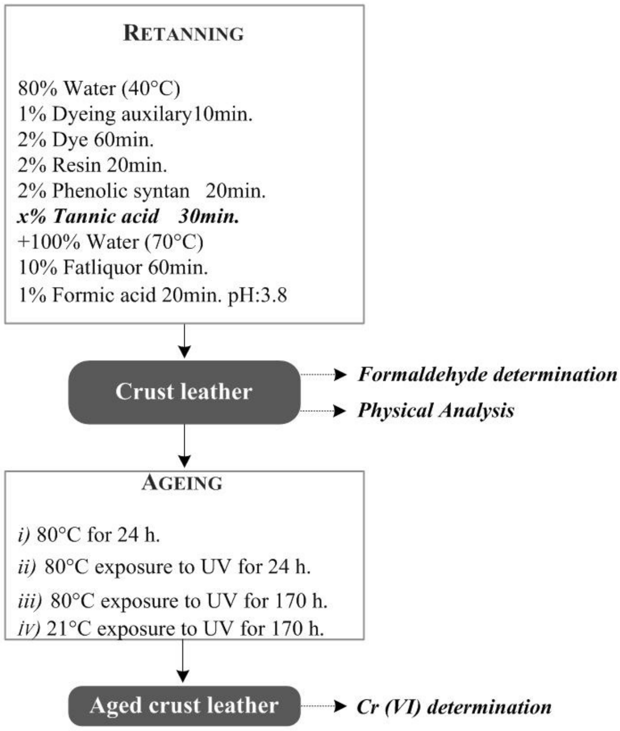

Figure 1. Flow diagram of the tannic acid treatment procedure (Tannic acid concentrations, x: 0.1, 0.5, 1, 2, and 3%)

Sixth group was considered as control and retanning processes were carried out in parallel by applying the same formulation without adding tannic acid. Following the physical analysis and determination of formaldehyde content of finished leathers in each group, samples were exposed to ageing process prior to chromium (VI) analysis. All analysis were performed in triplicate and given in mean values.

2.3 Determination of free formaldehyde

The free formaldehyde content of samples from control and tannic acid experiment was quantified in accordance with ISO TS 17226 standard method, using C 18 column and acetonitrile/water as mobile phase with a flow rate of 1.0 ml/min, at UV detection wavelength of 340nm (20).

2.4 Analysis of physical characteristics

The samples of standard dimensions were cut and conditioned by following TS EN ISO 2418 and TS EN ISO 2419 procedure (21,22). The physical properties such as tensile strength, % elongation at break and double edge tear load were investigated with reference to TS 4119 EN ISO 3376 and TS EN ISO 3377-2 standard methods (23,24). The shrinkage temperature, which is a measure of hydrothermal stability of leather, was determined as per TS 4120 EN ISO 3380 method (25).

2.5 Determination of hexavalent chromium

Oxidation of chromium (III) to chromium (VI) by air in production processes carried out at high pH, heat and irradiation with UV light were suggested as possible causes of the formation of hexavalent chromium in leather (6,26).

Tannic acid treated leather samples are subjected to accelerated ageing conditions, such as high temperature and UV light (340 nm) in a heat-adjustable UV cabinet for different time intervals, in order to facilitate the formation of higher amount of chromium (VI) in leather. For this purpose, control group and tannic acid treated leather samples were exposed to *i)* 80°C for 24 hours, *ii)* 80°C and UV for 24 hours *iii)* 80°C and UV for 170 hours, and *iv)* natural light at 21°C for 170 hours by avoiding direct contact with solar rays. After artificial ageing process, the determination of chromium (VI) content on leather samples treated with various concentrations of tannic acid was performed according to TS EN ISO 17075 standard procedure (27). This analytical method is based on the reaction of chromium (VI) with diphenylcarbazide and subsequent colorimetric determination at 540 nm by using a double beam Shimadzu 1601 UV visible region spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Effect of tannic acid on elimination of free formaldehyde

Figure 2 shows that free formaldehyde removal efficiencies increase as tannic acid concentration increases. In the control samples to which no tannic acid was added, formaldehyde content was detected as 44.9 mg/kg. 0.1%TA samples were found to be the highest formaldehyde containing samples at about 39.9 mg/kg. For offer of 0.5, 1 and 2% tannic acid, mean formaldehyde contents were found as 37.9, 32.6 and 29.1 mg/kg.

The maximum formaldehyde removal rate 45.3% was achieved by using 3% tannic acid in retanning process, which is higher than previously reported values 35% and 28%, obtained by Bayramoğlu et al. (13,14) in retanning process, with an offer of 4% hazelnut shell and 4% Camellia sinensis extract respectively.

3.2 Physical characteristics of leather

The physical characteristics of leather samples retanned with 0.1, 0.5, 1, 2, 3% tannic acid were evaluated. The summary of results obtained from tensile strength, elongation at break, tear load and shrinkage temperature analysis were given in Figure 3.

A marked improvement effect on the physical characteristics of leather in direct proportion to tannic acid offer was observed. The tensile strength values of leather samples were found above the acceptable 10N/mm^{2}value. Control samples provided the minimum value being 12, 7, until it reached to 17.8 N/mm^2.

As can be seen from Table 1, elongation values are within the range of the upper limit of 60% as indicated by UNIDO. Tear load values conform the standards with values higher than 15N/cm, and the lowest shrinkage temperature was determined as 107°C for control samples, whereas 100°C is acceptable as indicated in literature (28).

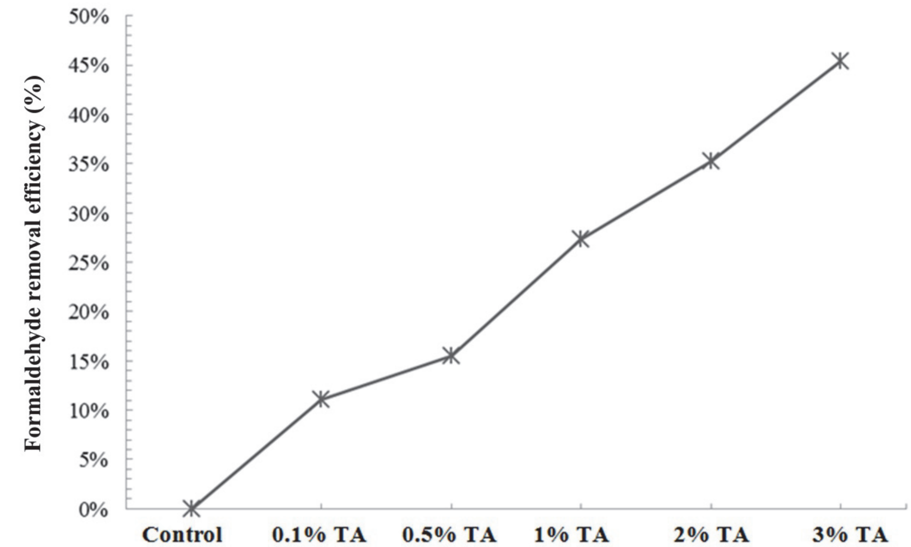

Figure 2. Effect of tannic acid concentrations on removal efficiency of free formaldehyde

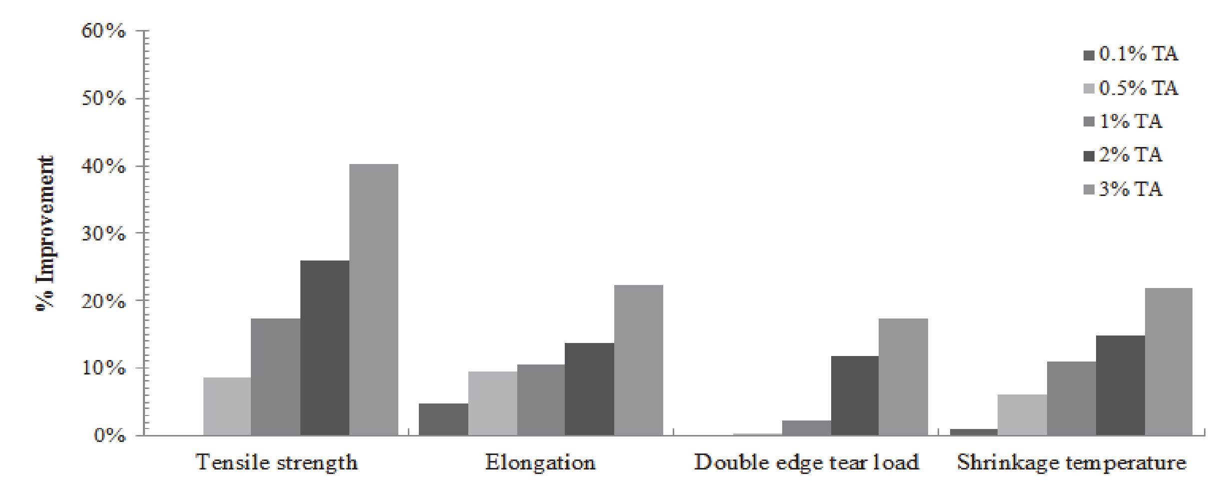

Figure 3. Improvement of tensile strength, tear strength and shrinkage temperature following the tannic acid treatment

Table 1. Physical characteristics of the samples

	Tensile strength (N/mm^2)	Elongation (%)	Tear Load (N/cm)	Shrinkage temperature (°C)
Control	12.7±4.0	40.5±13.8	30.6±6.5	107.3±1.9
0.1% TA	12.7±4.9	42.4±7.5	29.5±3.2	108.3±3.0
0.5% TA	13.8±1.7	44.3±7.5	30±8.7	113.8±5.4
1% TA	14.9±3.4	44.8±8.1	31.3±2.3	119±1.2
2% TA	16±2.2	46.1±8.3	34.2±3.8	123.3±1.8
3% TA	17.8±2.5	49.5±7.4	35.9±5.9	130.8±1.3

3.3 Effect of tannic acid concentrations on chromium (VI) formation

Heat and ultraviolet light are the predominant energy forms that come under consideration to provide the energy required for the oxidation of chromium (III) to chromium (VI). The inhibitory efficiency of various concentrations of tannic acid on chromium (VI) formation after exposure to UV light and thermal ageing for different time intervals was presented in Figure 4.

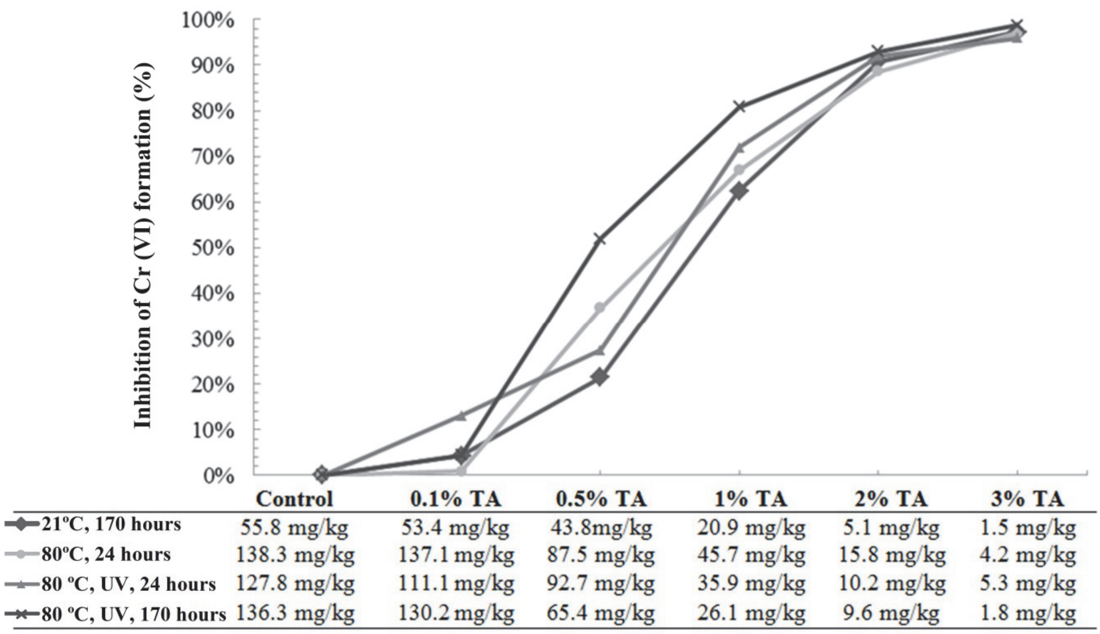

Figure 4. Inhibitory effect of tannic acid on chromium (VI) formation

As can be seen from the figure natural light has similar effect to those of UV light in terms of chromium (VI) formation. These results are analogous with the findings of Font et al. (6), in which approximately 65 mg/kg of chromium (VI) was obtained from naphthalene sulfonic acid retanned leather samples exposed to natural light for 8 days. In a similar way to previous studies the concentration of chromium (VI) in leather samples increased as the ageing conditions become more drastic (6,14,26,29).

Exposure to heat and UV for 170 hours had a significant effect on the formation of the chromium (VI) content in control samples, where concentrations up to 138.3 mg/kg was observed. Font et al. (26) reported Cr (VI) concentrations of 40 mg/kg after exposing un-retanned leathers to UV light for 325 hours. The type of retanning agent is also found to be significant on the formation of chromium (VI). Leather samples retanned with an offer of 6% mimosa, quebracho, sulfone and melamine dicyandiamide retanning agent yielded <1 mg/kg, <1 mg/kg, 36 mg/kg and 56 mg/kg Cr (VI), after exposure to UVA light for 170 hours (6). As can be seen from the results obtained by other authors, although considerable variation has been observed depending on the type of retanning, fatliquoring and ageing process, the findings are qualitatively comparable, likewise they exhibited the same pattern in which, leather samples without initial content of Cr (VI) produce considerable amounts of chromium (VI) after exposure to high temperatures and UV.

Tannic acid showed higher inhibitory effect on chromium (VI) formation at concentrations above 1% TA offer. The highest reduction was obtained with 3% TA offer with all ageing conditions, which is up to 98% in comparison to control group. Higher chromium (VI) concentrations are expected with exposure to UV and longer exposure times. However with increasing concentrations of tannic acid better removal efficiencies were obtained. Thus, tannic acid provides a very effective antioxidant protective effect on leather. The protective effect of tannic acid may be attributed to its capacity to absorb ultraviolet light with a peak of maximum absorption spectrum below 250 nm (30).

At 21°C and at 80°C accompanied with 170 hours of UV exposure ageing conditions, 3%TA samples complied by the detection limit of the ecolabel criteria for footwear and provided lower chromium (VI) values than 3 ppm.

4. CONCLUSION

This study focused on the investigation of antioxidant effect of tannic acid on hexavalent chromium and formaldehyde formation in leather. For this matter, tannic acid was used in various concentrations at retanning process, and its antioxidant effect has been demonstrated.

Tannic acid utilization at an offer higher than 1% at retanning within the existing leather production processes could be effective in maintaining the Cr (VI) content within the certain limits, while the 3% TA offer retained the values under the limit values up to 170 hours of UV and heat exposure. The retanning process with all concentrations of tannic acid used in the study provides an effective antioxidant inhibitory action for free formaldehyde on leather. Additionally, it has positive effects on physical characteristics of leather. The results indicate that tannic acid can be a natural additive in leather processing steps with multiple inhibitory functions, as the presence of chromium (VI) and formaldehyde in leather is a subject of considerable interest in the leather industry.

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