POLYMERIC COATINGS CONTAINING ANTIOXIDANTS TO IMPROVE UV AND HEAT RESISTANCE OF CHROME-FREE LEATHER

by

CHENG-KUNG LIU,* NICHOLAS P. LATONA, GARY L. DIMARO, AND PETER COOKE

United States Department of Agriculture, ** Agricultural Research Service,
Eastern Regional Research Center
600 EAST MERMAID LANE
WYNDMOOR, PA 19038-8598

ABSTRACT

For automotive upholstery leather, UV and heat resistance are very important qualities, particularly for non-chrome-tanned (chrome-free) leather. One of our research endeavors has focused on an environmentally friendly finishing process that will improve the UV and heat resistance of automobile upholstery leather. Both tocopherol and butylhydroxytoluene (BHT) are well-known antioxidants commonly used in the cosmetic and food industries. Tocopherol has been reported as a potent free radical scavenger and highly protective agent for collagen fibers against UV and heat damage. Experiments were conducted by adding 1 to 5% alpha-tocopherol and mixed-tocopherol to the grain layer finishes (topcoat) of chrome-free leather. The treated samples were exposed to artificial sunlight at a high temperature for 72 hours and then evaluated for the efficacy of UV and heat resistance and by mechanical property testing for tensile strength and fracture energy. Tests using 5% alpha-tocopherol or mixed-tocopherol showed a significant improvement in color fading resistance against UV radiation and heat. We also studied the addition of BHT to the fatliquoring drums. Observation, however, showed BHT has no beneficial effect on the UV and heat resistance of finished leather.

RESUMEN

Para tapicería automotriz, las propiedades de solidez al calor y la radiación ultravioleta (UV) son muy importantes, sobretodo para curtidos libres de cromo. Una de nuestras líneas de investigación se ha enfocado en acabados eco-benignos que mejoren las resistencias al calor y UV en cuero para tapicería automotriz. Tanto tocoferol como butilhidroxitolueno (BHT) son antioxidantes bien reconocidos y comúnmente utilizados en las industrias de productos cosméticos y de comestibles. Tocoferol se ha reportado como un potente recolector de radicales libres y agente protector de fibras de colágeno contra UV y deterioro térmico. Experimentos se efectuaron añadiendo de 1 a 5% de alfa-tocoferol o mezclas de tocoferoles, al acabado de flor para cueros exentos de cromo. Las muestras así tratadas fueron expuestas a luz solar artificial a temperatura elevada durante 72 horas y luego evaluadas por su eficacia en resistir UV y calor, como también comprobar las propiedades físicas de resistencia a la tracción y energía de fracturación. Pruebas utilizando 5% de alfa-tocoferol o mezclas de tocoferoles demostraron significante mejoria en solidez del color a radiación UV y calor. También se estudió la adición de BHT a los fúlones de engrase. Sin embargo no se detectó que el BHT tuviera algún efecto benéfico sobre la resistencia al UV y calor en cuero terminado.

INTRODUCTION

Although the leather industry is still largely using chromium (III) salts as tanning agents, environmental concerns over the use and disposal of chrome-tanned leather have increased the demand for chrome-free leather, particularly in the European automotive leather markets. Presently there is also an increasing demand for the domestic production of automotive leather. In some respects, the quality of chrome-free leather such as glutaraldehyde-tanned leather is inferior to that of chrome-tanned leather, for example in colorfastness and thermal stability. Leather for car interiors is required to meet exceptionally high quality standards. Consumers expect leather to be able to withstand exposure to extreme and varying temperatures, light, moisture and mechanical loading conditions over time. Most automobile leather is colored to improve its appearance and aesthetic value. Sunlight, on other hand, is a powerful form of energy that can decompose the chromophores into smaller pieces and can cause a yellowing or bleaching effect. The poor lightfastness of crust leathers prevents the use of light pigments or dyes and, therefore, more natural looking or aniline finishes for leather are difficult to
achieve. When using such leather in automotive applications, these inadequacies need to be studied to find ways of producing lightfast leather with improved thermostability.

Many studies have demonstrated physico-chemical changes of collagen induced by UV radiation. Sionkowska reported that solar radiation induces photodegradation of collagen. Fujimori revealed that a solution of collagen, after UV irradiation, loses the ability to form natural fibrils. For synthetic polymers, UV absorbents such as hydroxybenzophenones have been widely used to improve the light stability of both plastics and their colorants. UV absorbents are also commonly used in skin care products such as sunscreens. They include benzophenones, cinnamates and salicylates. Contact sensitivity or allergic reactions have been reported with benzophenones. Cinnamates are effective UV blockers but having poor waterproofness. They are generally used in combination with other agents; an example is octylmethyl cinnamate. Salicylates are also often used in sunscreens, and they are water-insoluble. Antioxidants are often included in sunscreens as free-radical scavengers. Tocopherol is a potent free radical scavenger and a highly protective agent against UV skin damage. It is a light yellow colored fat-soluble vitamin. The principal role of tocopherol as an antioxidant must be to neutralize free radicals and prevent a chain reaction in the formation of peroxides or other products due to their subsequent degradation. Thermal stability of leather may be improved by using antioxidants such as tocopherols to protect against thermal oxidation, thereby improving the stability of the triple helical structure of collagen molecules. The current study focuses on non-chrome-tanned leather made with a glutaraldehyde tanning process. Glutaraldehyde tanning was developed by Filachione et al. in the Eastern Regional Research Center (ARS, ERRC) in the early 1960s. It has become the most common alternative tanning agent to chrome salts, because it is less expensive, is readily available and is highly soluble in aqueous solution. In recent years, it has been the dominant tanning agent for the preparation of chrome-free leather. The chemistry of fixation of glutaraldehyde to collagen is not fully understood. Presumably, it involves crosslinking by the reaction of an aldehyde group with an amino group of lysine or hydroxylysine or an aldol condensation between two adjacent aldehydes.

In the early phase of this project, we applied alpha-tocopherol to the grain layer of leather and also studied the addition of tocopherol to the fatliquoring process. Following exposure in a Fade-Ometer, the treated samples were evaluated by colorimetry and mechanical testing for the efficacy of UV- and heat resistance. Data showed that coating leather with alphatocopherol significantly improves the color fading resistance and strength retention against UV radiation and high temperature. A polarizing microscope equipped with a Berek compensator was employed to determine the birefringence of the untreated and treated leather collagen fibers to determine the treatment effects on the degree of orientation. Data showed that leather coated with tocopherol exhibited significant improvement in tensile strength retention and color fading resistance against UV radiation and heat. We also studied the addition of tocopherol to the fatliquoring drums, but this treated leather did not show a similar improvement. More recently, we carried out a study to gain a better understanding of how environmental factors affect the colorfastness and mechanical properties of chrome-free leather. Data showed that an increase in radiation dosage and temperature have a detrimental effect on the colorfastness of dyestuff and mechanical properties of leather. Observation, however, showed an intriguing interaction between the levels of humidity and radiation dosage. Measurements revealed that an increase in humidity resulted in a higher delta E value, an indication of decreased colorfastness, and a decrease in tensile strength. However, after the UV radiation dosage reaches a certain level, an increase in humidity may actually help maintain both properties. Observation showed the stiffness decreased steadily with an increase in humidity, whereas the toughness increased slightly with increasing levels of humidity. Using differential scanning calorimetry, we observed a correlation between colorfastness and the denaturation temperature. This finding implies that the factors that break the molecular chains of colorants are also strong enough to break the bonding of the collagen molecules. The knowledge obtained from this research may benefit the leather industry in better understanding the environmental effects on chrome-free leather, thereby tailoring the leather-making process to meet quality specifications. Moreover, the information provided by this research could lead to a proper formulation of antioxidants to apply to leather for improving the resistance to deterioration due to environmental changes.

Finishing is a process to apply film-forming materials, so-called "coatings" on the grain surface to provide abrasion and stain resistance and perhaps more importantly, to beautify the leather. It is also the last step to cover any minor surface defects such as small scratches and cracks. The specific steps in the finishing process are dependent on the requirements of the final product. Full grain leathers typically have a polymeric finish applied to the grain surface by a roller coater or a spray gun. Corrected grain leathers have one or more basecoats applied, which improves the adhesion of the final topcoat; the topcoat is then applied and dried. In all the previous studies, tocopherol was either coated on naked skin (crust) or added in the fatliquoring bath; the samples were not treated with polymeric coatings. The reason for this is that we wanted to observe the interaction of tocopherol with leather. This report describes our experiments that were conducted with adding 1 to 5% alphatocopherol and mixed tocopherol to the grain layer finishes of chrome-free leather. The treated samples were exposed to artificial sunlight at high temperature and then evaluated for the efficacy of UV and heat resistance and by mechanical property testing for strength and stiffness. Butylhydroxytoluene (BHT) is a well known antioxidant that has been widely used in the food industry. Recently, ERRC's scientists also reported that the addition of BHT (1000 ppm) reduced NOx emissions from B20 biodiesel (20% soy biodiesel/80% diesel fuel blend) exhaust. Thus, we also studied the addition of BHT to the fatliquoring drums. Following exposure in a Fade-Ometer, the treated samples were evaluated by colorimetry and mechanical testing for the efficacy of UV and heat resistance.
The experimental topcoats were manually applied 2 times at -1.1 g/ft² for each pass. The pieces were then allowed to air dry overnight before being placed into a constant temperature/humidity room. Next, 14- x 6.5-cm samples were cut out of the finished leather to fit into the Fade-Ometer. Figure 2a shows that a thin layer of coating film is formed on top of the grain. More details can be observed from Figure 2b, which is a magnified SEM micrograph for this coating, and which shows a sponge-like texture and is about 30 µm thick. The samples were then placed in a Fade-Ometer, set at 225.6 kJ/m² measured at 420 nm. The experiment was done in duplicate on each side of 1 hide.

### Measurements

Mechanical property measurements included tensile strength and fracture energy. Tensile strength is the maximum stress in tension that the leather may sustain without breaking. Fracture energy is defined as the energy needed to fracture leather samples. This physical quantity is sometimes mentioned as "toughness". Rectangular shaped leather samples (1- x 10-cm) were cut near the standard test area as described in ASTM D2813-97 with the long dimension parallel and perpendicular to the backbone. These properties were measured with a sample length of 5 cm between the two grips. The strain rate (crosshead speed) was set at 5 cm/min. An upgraded Instron mechanical property tester, model 1122, and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Each test was conducted on four samples to obtain an average value.

We used an Atlas Ci3000F, Xenon Arc Fade-Ometer (Oxford, PA), to evaluate the UV- and heat resistance of the leather samples. The samples were put inside the Fade-Ometer that had been calibrated at 420 nm, for a total radiation dosage of 225.6 kJ/m² (about 72-h exposure). The settings for the Fade-Ometer were as follows (DIN 75202): black panel temperature 100 ± 2°C, dry bulb temperature 65 ± 5°C, radiation intensity 1.1 Watts/m², and RH 20 ± 10%. These settings have been commonly used in various industries for testing UV and heat resistances. The colorfastness to light of the specimen is evaluated by measuring the color change (ΔE) between the exposed samples and the unexposed original samples, using the color-insights® QC Manager System (BYK-Gardner, Inc., Silver Spring, MD), which is an absorptiometric colorimeter often used for fabrics. We followed the CIELAB colorimetric method; DE was calculated using the equation:

$$
\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}.1/2
$$

\Delta L represents the difference between
light and dark. $a^*$ represents the difference between green ($-a^*$) and red ($+a^*$), and $b^*$ represents the difference between yellow ($+b^*$) and blue ($-b^*$). Measurements were conducted four times to obtain an average value.

**Environmental Scanning Electron Microscopy**

To examine the effects of treatments on the fibrous structure of the leather samples, we used the field-emission environmental scanning electron microscope (ESEM) to examine the cross section of the leather samples. ESEM is advantageous over conventional scanning electron microscopy because a relatively high vacuum in the specimen chamber is not needed to prevent atmospheric interference with primary or secondary electrons; an ESEM may be operated with a poor vacuum (up to 1.3 kPa of vapor pressure, or one seventy-sixth of an atmosphere) in the specimen chamber. Our ESEM was operated at low vacuum (40 Pa) with the voltage set at 15 kV, spot size 5.0 and working distance of approximately 10 mm. The samples were not sputtered with either gold or carbon coatings, thus preserving the original characteristics of the leather samples.

**Cyclic Tensile Tests and Hysteresis Measurements**

We programmed the tensile tester (Instron mechanical property tester) to perform a cyclic test, which was designed for measuring the hysteresis of leather samples. Rectangular-shaped leather samples were cut near the standard test area as described in ASTM D2813-97 with the long dimension parallel to the backbone. Sample size was 10- x 1-cm with a moisture content of 18±1%. Samples were loaded into the jaws and they were then stretched to 0.3 kgf (0.94 N force) to eliminate the slack and start the samples all at the same pretension. At 0.3 kgf the cross head was zeroed to 0% strain and the samples were stretched to 20% strain at 50mm/min and then back to 0% strain; once 0% strain was reached the samples were again stretched to 20% strain and then back to 0% strain. A total of 5 cycles were tested and the loading, unloading, and hysteresis (which is calculated by subtracting unloading energy from loading energy) were recorded for each cycle as well as the peak stress and elastic (Young’s) modulus.

![Figure 3: Color change. Abbreviations: M.Toco. = Mixed-Tocopherol; Toco. = Alpha-Tocopherol.](image)

![Figure 4: SEM micrographs; (a) no tocopherol (b) mixed-tocopherol (c) alpha-tocopherol](image)

![Figure 5: Stereo micrographs; (a) no tocopherol (b) mixed-tocopherol (c) alpha-tocopherol](image)
UV AND HEAT RESISTANCE

RESULTS AND DISCUSSION

Color Lightfastness
The Delta E value was measured for each of the samples. The Delta E value reported is an average of the parallel and perpendicular samples for a total of 4 specimens. As can be seen in Figure 3, the Delta E value for the control is significantly higher than the treated samples; the 5% mixed- and alpha-tocopherol have a much lower Delta E, compared to the controls. Coatings with 5% tocopherols have done a better job preserving the color, measured with the colorimeter.

Effects on Surface
Figure 4a is an ESEM micrograph of the sample without tocopherol, whereas Figures 4b and 4c are from the coatings 5% mixed-tocopherol and alpha-tocopherol, respectively. It is quite clear that adding mixed- or alpha-tocopherol led to much less deterioration than observed in the samples without tocopherol. Similarly, Figure 5a showed more damage on the grain than the samples with tocopherol in Figures 5b and Figure 5c. UV-induced grain crack was reported in our previous paper illustrated by micrographs; the high-dose irradiated leather showed severe cracks; in contrast, the un-irradiated leather showed much more of a smooth grain surface.

Tensile Strength and Fracture Energy Retentions
Graphs of the Tensile Strength Retention ratio (Figure 6a), show a significant difference between the control and coatings with tocopherol; in particular, for strength retention, the 5% mixed-tocopherol (M.Toco) and alpha-tocopherol (Toco) samples showed great retention. The retention calculations are obtained by dividing the tensile strength or fracture energy values after irradiation with the values with no irradiation. Therefore a number of 1 would indicate there was no change in the value after irradiation. As we can see, the 1% tocopherol yielded little improvement. The Fracture Energy Retention Ratio (Figure 6b) shows the control has the lowest retention ratio.

BHT Treatments
A set of experiments was also conducted by adding butylhydroxytoluene (BHT)--2,6-bis(1,1-dimethylethyl)-4-methylphenol) to the fatliquoring drum. The additions consisted of 0, 0.5, 1, 2, 5 and 10% by weight of BHT to the fatliquor (EUREKA 950-R, a low fogging oil based on an

Figure 6: (a) Tensile strength retention, (b) fracture energy retention. Abbreviations: M.Toco. = Mixed-Tocopherol; Toco. = Alpha-Tocopherol.

Figure 7: Color change as a function of BHT offered in fatliquoring drum.

Figure 8: Tensile strength as a function of BHT offered in fatliquoring drum.
Cyclic Stress-Strain Behavior

As shown before, tocopherol yields beneficial effects on the UV- and heat resistance. We were interested to know whether tocopherols also produce a different viscoelasticity in the leather compared to the control samples after UV irradiation. Cyclic tensile tests were designed to answer this question. We previously reported that cyclic tensile tests provide insight into the difference between non-milled and milled leather.27 The same tests were also performed to probe the structural difference between chrome-tanned and chrome-free leather tanned with glutaraldehyde.28 Figure 9 displays the non-treated and treated leather samples' 5-cycle stress-strain curves. We see in general that the tocopherol-treated samples (Figure 9b) have a smaller hysteresis (energy loss) than the non-treated leather (Figure 9a), i.e., a smaller initial slope, and lower peak stress. Moreover, as shown in Figure 10, the control samples (a) have a higher stress peak compared to the tocopherol-treated leather samples (b). We believe this is because the fibers in the control leather have a higher stiffness compared to the fibers in the treated leather. Therefore more stress is produced when the control samples are stretched.

Stress Relaxation Experiments

Fibrous materials such as leather generally demonstrate a mechanical behavior that may incorporate a blend of both elastic and viscous characteristics; this is referred to as viscoelastic behavior.29-31 We previously reported that besides the elasticity, the viscous component or viscosity plays an important role in determining the stress-strain curve even at the very beginning of the leather deformation.29 The viscoelasticity is commonly measured by either dynamic or static tests.32 In the dynamic tests, a sinusoidal variation of strain is imposed to the material...
and a variation of the responding stress is observed. In the static tests (our current test), a constant strain or a constant stress is imposed, and the variation of the stress (relaxation) or the strain (creep) as a function of time is observed.

We performed stress relaxation experiments in this study. The samples were stretched to 20% strain and then held at this constant strain for 10 minutes (600 sec). Figure 12 shows the stress as a function of time, for both the control and treated leather. It clearly shows that for all three samples, the stress starts to decay as time passes. This behavior is beneficial for gaining comfort in an initial deformation as leather contacts the human body. However, if the relaxation is too much or the sample does not return to its original shape after the stress is released, then it may create bagginess. It is worth to note that the Figure 12 data curves look undulated; it may be possibly due to the fiber movements in the leather. Leather is a fibrous material consisting of interwoven fibers. Fibers may have small scale local movements under a constant strain (20%) and lead to stress fluctuations, which can be detected by a very sensitive load cell. This behavior may not normally be seen in non-fibrous materials such as polymeric films.

The stress-relaxation behavior as shown in Fig. 12 is associated with the viscoelasticity of leather. Generally, the linear viscoelastic models for the static tests, are developed from two elements: a spring (elastic) and a dashpot (viscous), as shown in Fig. 13. Theoretically the first element works according to Hooke’s law (stress is proportional to strain), and the second element obeys Newton’s law (stress is proportional to the speed of strain, or strain rate). A spring and a dashpot in series constitutes the model of Maxwell (Fig. 13a), and in parallel the model of Kelvin or Voigt (Fig. 13b). These are the simplest models based on the theory of linear viscoelasticity. For stress-relaxation, the Maxwell model has been commonly used for the elucidation of data. Assume leather is stretched to a total strain, \( \varepsilon \); the total strain is the sum of elastic strain, \( \varepsilon_e \) and viscous strain, \( \varepsilon_v \), as shown in Equation 1.

\[
\varepsilon = \varepsilon_e + \varepsilon_v \tag{1}
\]

For elastic bodies, the stress is proportional to strain and the ratio is the elastic modulus (G) (Equation 2). On the other hand, for viscous flow, the stress is proportional to the rate of strain (Equation 3), where \( \eta \) is the viscosity. If we take the differential of Equation 1 against time, we can obtain Equation 4. The solution for Equation 4 can be written as Equation 5,

\[
\sigma = G \varepsilon_e \tag{2}
\]

\[
\sigma = \eta \left( \frac{d\varepsilon_e}{dt} \right) \tag{3}
\]

\[
\frac{d\varepsilon_e}{dt} + \frac{d\varepsilon_v}{dt} = \frac{d\sigma}{dt}/G + \alpha/\eta = 0 \tag{4}
\]

\[
\sigma(t) = \sigma_0 e^{-t/(G/\eta)} = \sigma_0 e^{-t/\tau} \tag{5}
\]

where \( \tau \) is the time needed for the stress to decay to the 1/e of the initial stress, \( \sigma_0 \), the so-called relaxation time. It is an important parameter related to the viscoelasticity of a material. According to Equation 5, it is easy to see that \( \tau \) equals \( \eta/G \), where \( \eta \) is the viscosity and \( G \) is the elastic modulus. To estimate \( \tau \), we can take the natural log against both sides of Equation 5 to obtain the following equation:

\[
\ln \sigma(t) = \ln \sigma_0 - \frac{t}{\tau} \tag{6}
\]
\[
\ln \sigma(t) = \ln \sigma_0 - (t/\tau)
\]

One then can perform a linear plot \(\ln \sigma(t)\) against \(t\); the resultant slope will be \((-1/\tau)\) and the intercept will be \(\ln \sigma_0\), as shown in Figure 14a. The relaxation time can be calculated according to Equation 7.

\[
\tau = t/(\ln \sigma_0 - \ln \sigma(t))
\]

However, as demonstrated in Figure 14a, the data did not fit well to the Maxwell model. A similar problem was reported by Komanowsky et al. for chrome-tanned shoe upper leather.\(^{34}\)

To achieve a better fit for the stress-relaxation data, they used a composite model having 3 Maxwell elements in parallel. This model is rather complicated, in that it has 3 different viscosities and elastic moduli, and consequently 3 different values of \(\tau\). We designed a simplified model, assuming that the rate of stress \((\text{d} \sigma(t)/\text{d}t)\) is a linear function of reciprocal time \((1/t)\), which is inversely proportional to \(t^{-1}\) as shown in the following equation:

\[
\frac{\text{d} \sigma(t)}{\text{d}t} = -\beta t^{-1} \quad (t \geq 1)
\]

where \(\beta\) is a constant associated with the viscoelasticity of leather. Time must be greater or equal than 1; there is no solution for Equation 8 when \(t = 0\); however, we observed that the difference between \(\sigma_0\) and \(\sigma_f\) is negligible as shown in our experiments. Consequently the solution of Equation 8 can be obtained as follows:

\[
\sigma(t) = \sigma_f - \beta \ln(t) \quad (t \geq 1)
\]

The relaxation data fit this model rather well, as shown in Fig. 14b. It is worth to note that there is a fast decay in stress in the first minute. This behavior actually helps in the period to break in shoes or gloves and provide a better comfort and fit for the leather products. Hereafter, the stress relaxation significantly slows down and becomes flat, thereby preventing the baggy feeling. The tocopherol samples as can be seen in Figure 14b have lower stress-relaxation curves compared to the control. The \(\sigma_f\) value in Equation 9 is related to the stiffness of a material and therefore if we compare the three curves the alpha tocopherol has a very low \(\sigma_f\) value. On the other hand, \(\beta\) is associated with the stability of the leather and indicates that the alpha-tocopherol sample, which has a lower \(\beta\) value, is more stable and softer after UV exposure than the control sample.

**Conclusions**

This on-going research aims to develop a process treatment that is environmentally friendly and yet significantly increases the UV and heat resistance of chrome-free leather. This study showed that 5% alpha-tocopherol or mixed-tocopherol works well as UV-resistant additives to topcoats for chrome-free leather. It appears that BHT does not improve properties of the UV-treated leather. We designed a cyclic tensile test to measure the hysteresis and gain insight into the structural difference between the control (untreated) leather and tocopherol-treated leather. Observations revealed that untreated leather has a relatively higher hysteresis than treated leather. This indicates that the treated leather structure is more stable than untreated leather toward UV radiation. The stress-relaxation experiments, on the other hand, indicated that untreated leather is relatively stiffer than treated leather. In this study, we also formulated a linear stress rate model to predict the time-dependence of stress-relaxation, which fits the data better than the traditional Maxwell model. Moreover, observations showed the viscoelasticity of leather was affected significantly by the tocopherol treatments. Tocopherol added to the topcoat increased the protective function and resulted in a softer leather.

**Acknowledgments**

We thank Mrs. Guoping Bao of ERRC for SEM photos. We also thank Dr. David Coffin of ERRC and Mr. James Haworth of Cargill Health and Nutrition for their invaluable information and comments. We would also like to thank Mr. Bob Smith of Quakercolor for his valuable input regarding leather coatings.
REFERENCES


