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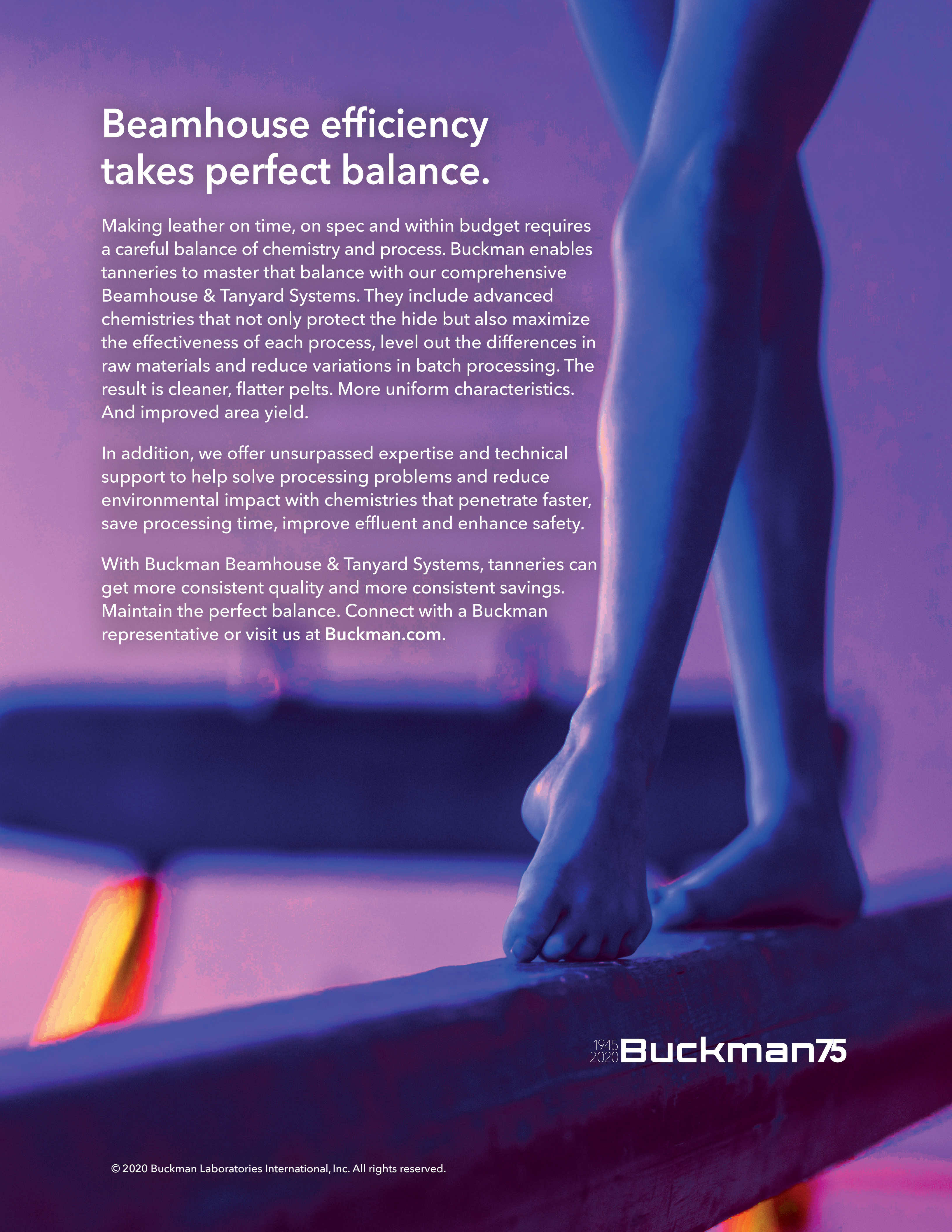

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Application of L-Ascorbic Acid as an Antioxidative Colorment in Leather Finishing

by

Sultan Çivi and Eser Eke Bayramoğlu*

Ege University, Faculty of Engineering, Department of Leather Engineering, 35100 Bornova-İZMİR – TÜRKİYE

Abstract

In this study, chrome tanned bovine crust leathers were dyed white during finishing process. Experiments with 1%, 2%, 3%, 4% and 5% L-ascorbic acid addition were performed on the finishing layer of the finishing application. L-ascorbic acid was not added to the control group and processed according to the standard method. After these processes, color measurement analyzes were performed on Konica Minolta CM 3600d spectrophotometer. In order to investigate the effects of L-ascorbic acid on other performance properties of leather, light fastness test according to TS 1008 EN ISO 105-B02 (2001 TS EN ISO 11640 2001) and dry rub fastness test according to standard method were performed. The results of the study were statistically evaluated according to the NCSS (Number Cruncher Statistical System) method. As a result of the research, it was observed that L-ascorbic acid gave a pearly pink color to the leathers. It was found that the dry rubbing fastness of the leathers treated with L-ascorbic acid improved. In the light fastness tests, the results of the experimental group leathers were recorded better by the blue scale.

Introduction

Leather production, which is a by-product of the meat industry, is a traditional industry that has existed since ancient times and using animal skin is one of the oldest technologies of humanity.[1] According to the final product (clothes, shoes, upholstery, saddlery etc.) chemical (soaking, unhairing-liming, deliming, bating, degreasing, pickle, tanning, basification, neutralization, dyeing, lubrication, retanning, finishing) and mechanical (fleshing, shaving, drying, ironing-press) covers a number of processes.[2,3] The desired surface properties (color, glossy or matt appearance, slippery, etc.) to the leather by the finishing process and the performance characteristics that provide protection against external factors (light fastness, rubbing fastness, resistance to solvents etc.) and become available for sale.[4] For this purpose pigments, aniline dyes, binders (acrylic, polyurethane, butadiene etc.), waxes, touching agents, lacquers (polyurethane, nitrocellulose), various organic solvents and cross-linkers (polyaziridines, isocyanates and polycarbodiimides) are used.[5,6]

L-ascorbic acid is a powerful water-soluble antioxidant.[7] It protects some oxidizable compounds with its reducing effects as free radicals and oxygen annihilator. L-ascorbic acid is used in skin care products in the cosmetic industry and as an additive in the food industry.[8,9]

Koochakzaei et al. in their research on the stability of silicone oil and polyethylene glycol; they used L-ascorbic acid to increase the effectiveness of polyethyleneglycol.[10] According to Devikawati et al. used ascorbic acid, gallic acid, tara, mirobalan and keratin-based protein hydrolyzate to prevent the carcinogenic effects of hexavalent chromium. The results of the research show that the use of Ascorbic acid during descaling, pickling and tanning is more effective in preventing the formation of hexavalent chromium.[11] Kothandam et al. synthesized nano-sized copper and used ascorbic acid as an oxidation inhibitor during copper synthesis in their study investigating the effects of this substance on leather performance properties in the finishing of shoe upper leathers. In addition, researchers state that ascorbic acid is generally used in nanotechnology applications during copper synthesis and storage.[12]

As can be seen from the above mentioned studies in the leather industry, L-ascorbic acid is not widely used. Leather production effect on the leather and chemicals used in the interaction is a subject that is open to research. Since it is a known fact that dyes, like most chemicals used in leather production, may have some harmful effects, alternative materials are needed. Therefore, in this study, it was aimed to benefit from coloring ability of L-ascorbic acid, which is known for its antioxidant properties.

Experiments

Finishing Applications

In this research, chrome tanned undyed bovine crust leathers were used. L-Ascorbic acid powder form used in experiments. Finishing recipe is shown Table I.

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*Corresponding author email: eser.eke@ege.edu.tr, eserekebay@gmail.com

Table I

Finishing recipe used in application

Chemicals	**Application** **1. Coat (grams)**	**2. Coat (grams)**	**Explantion**
Akral PU Soft	220		Mixture of acrylic and polyurethane binders (Alpa Kimya)
Ground Plus A	50		Synthetic wax (Alpa Kimya)
Akrederm 1193	100		Acrylic Binder (Alpa Kimya)
SFT-MV-1	85		Wax-polyamide mixture(Alpa Kimya)
RPU 2260	50		Polyurethane Binder(Stahl Kimya)
PP 25838	100		White pigment(Stahl Kimya)
HM 443	7	10	Silicone touch (Stahl Kimya)
Water	290	100	
LW 21016		100	Hydrolacs (Stahl Kimya)
L-Ascorbic Asid		X	

1) 6xspray- Roto Press(80°C, 150 Bar)-4xspray- Roto Press (80°C,70 Bar)-3xspray
2) 2xspray- Roto Press(90°C- 70 Bar)

After the first coat application of the finishing recipe, each leather divided into three parts. The amount indicated by X in the second coat solution, the total solution and 0%, 1%, 2%, 3%, 4% and 5% of the leathers were added. Each experiment has three replicates was carried out. All leathers are conditioned for reproducible tests in the laboratory under equal conditions (20 ± 2°C 65 ± 2% RH).

Dry Rubbing Fastness Analyses

Leather samples were tested with black colored felt and dry rub fastness tests according to TS EN ISO 11640 (2001) from the grain surface. Otto Specht Bally Finish Tester device used for analysis. Color changes in leather samples and felts were evaluated according to ISO 105-A02 (1996) and ISO 105-A03 (1996) standards and ISO 105 standard with Gray scale.

Color Measurement Tests of Leather Samples

Color fastness determination was realized on Konica Minolta brand CM 3600d Spectrophotometer. Firstly, Standard black and white calibration process was practiced in device. Measurement was carried out by reading 5 points (4 corner points and 1 mid-point) from the grain surface of the samples into the reading area of the instrument. The results were evaluated by averaging these 5 measurement sites.

Light Fastness Analysis

Light fastness determinations were analyzed according to TS 1008 EN ISO 105-B02 (2001) standard for 24 hours by ATLAS brand ALPHA model xenon arc light fastness test device. The results were evaluated with blue scale.

Statistical Evaluation of Results

While evaluating the findings of the study, statistical analysis NCSS (Number Cruncher Statistical System) 2007 Statistical Software (NCSS LLC, Kaysville, Utah, USA) was used. While evaluating the study data, Kolmogorov Smirnov test and boxplot graphs were used to evaluate the suitability of the quantitative data for normal distribution as well as descriptive statistical methods (average, standard deviation, median, frequency and ratio). Normal distribution of parameters between groups One-way Anova test and Bonferroni test for detecting the difference group; Student's t-test was used in their evaluations according to two groups. Between groups of non-normal distribution of parameters Wallis test and Dunn test in detecting the difference group; Mann Whitney U test was used in evaluations according to two groups. In comparison of qualitative data, Fisher Freeman Halton test was used. The results were evaluated at 95% confidence interval and $p < 0.05$ significance level.

Results and discussion

Results of the appearance of leather

The leathers were subjected to visual evaluation after the application. After the use of L-ascorbic acid, different tones from yellow to pink were observed in the leathers. Figure 1 shows these color differences.

Dry rubbing fastness results

In accordance with the standard method, dry rubbing fastness analysis of the leathers were made using black colored felts. The

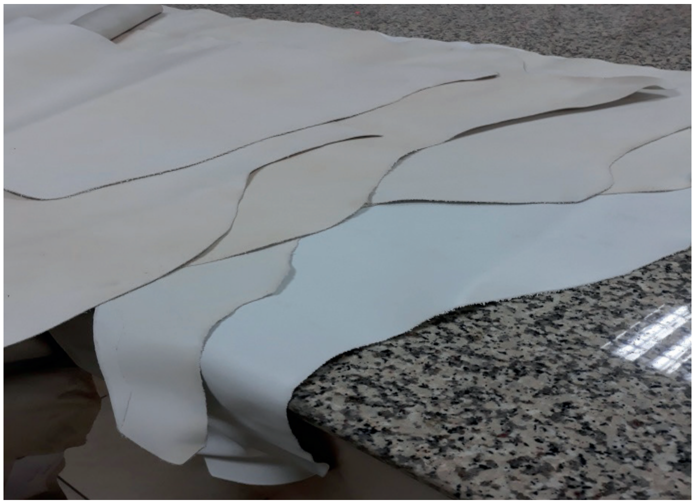

Figure 1. Color change observed in leather samples after finishing

results were evaluated on a gray scale. According to the results of both felt and leather color changes occurred between 1 and 5 points were given. A value of 5 indicates no spotting and a value of 1 indicates extreme spotting.

The results of dry rub fastness evaluation showed a statistically significant difference between leather and felt between control and experimental groups ($p < 0.01$). Dry rubbing fastness results were higher in the experimental group.

Color measurement analysis results

The color measurements will be evaluated according to DE * ab (D65) results obtained from L * a * b color areas measurements. Table III shows that color measurements evaluation results.

In our study, a statistically significant difference was found between the color measurements of the control and experimental groups ($p < 0.01$); D65 levels were significantly higher in the experimental group. D65, which is also a color criterion, showed statistically significant difference in the evaluation results according to L-ascorbic acid ratios in the experimental group ($p < 0.001$). There was no significant difference between 1% L-ascorbic acid and 2% L-ascorbic acid color measurements ($p > 0.05$); The D65 color value obtained in those using 1% L-ascorbic acid was significantly lower than those using 3% and 4% (p: 0.001; p: 0.001); There was no significant difference between 5% and 1% in color ($p > 0.05$).

Table II

Evaluation of dry rub fastness test results

		Control	Experimental		
		n(%)	**n(%)**	**Test Value**	**p**
Leather	3	3 (100)	0 (0)		
	4/5	0 (0)	3 (20)		
	5	0 (0)	12 (80)	11.889	0.002**
Felt	3/4	3 (100)	0 (0)		
	4	0 (0)	3 (20)		
	4/5	0 (0)	12 (80)	11.889	0.002**

Fisher Freeman Halton test **p<0.01

Table III

Color measurement evaluation results

	Control		Experimental	
	Median (min-max)	**Ort+SD**	**Median (min-max)**	**Ort+SD**
L*(D65)	93.3(90.9/94)	93.19±0.74	90(86.2/91.5)	89.6±1.24
a*(D65)	-1.1(-1.3/-1)	-1.09±0.06	1.1(-0.1/2.6)	1.18±0.75
b*(D65)	2.5(1.7/3.2)	2.44±0.3	9.3(6.1/15.4)	9.69±2.34
dL*(D65)	-4.9(-8/-2.9)	-4.66±1.25	-8.3(-12.6/-5.4)	-8.25±1.6
da*(D65)	-1(-1.2/-0.9)	-0.98±0.07	1.2(0/2.7)	1.29±0.75
db*(D65)	2.8(2/3.4)	2.74±0.3	9.6(6.5/15.7)	9.99±2.34
dE*ab(D65)	5.7(4.1-8.5)	5.54±1.05	12.3(8.8-20.2)	13.08±2.67

Table IV

Evaluation results of color measurements according to L-ascorbic acid ratio

			dE*ab(D65)			
		n	**Median (min-max)**	**Ort+SD**	**Test Value**	**p**
	Control	30	5.7(4.1/8.5)	5.54±1.05		
Group	Experiment	150	12.3(8.8/20.2)	13.08±2.67	15.165	[a]0.001**
					58.55	[b]0.001**
						Post Hoc;
						%1-%3 p:0.001
						%1-%4 p:0.001
	1% L-Askorbic Asid	30	12.1(9.2-15.8)	12.16±1.53		%2-%3 p:0.001
	2% L-Askorbic Asid	30	11.3(8.8-14.6)	11.41±1.42		%2-%4 p:0.001
	3% L-Askorbic Asid	30	17.2(10.7-20.2)	16.75±2.39		%3-%4 p:0.001
	4% L-Askorbic Asid	30	14(9.8-17.1)	13.98±1.61		%3-%5 p:0.001
L-Askorbic Asid	5% L-Askorbic Asid	30	10.9(9-13.4)	11.08±1.18		%4-%5 p:0.001

[a]Student t test [b]Oneway Anova test & posthoc Bonferroni test **p<0.01

D65 color measurements were significantly lower in 2% L-ascorbic acid use compared to 3% and 4% (p: 0.001; p: 0.001); No significant difference was found between 2% and 5% (p> 0.05). The use of 3% found the highest D65 color measurement and was significantly higher than 4% and 5% (p = 0.001; p: 0.001). Color measurements obtained by using 4% L-ascorbic acid were found to be significantly higher than 5% usage.(P = 0.001).

Light fastness test results

Table V shows the results of light fastness analyzes. Evaluation of blue scale used in light fastness test results showed statistically significant difference between control and experimental groups (p <0.01). The results of experiments evaluation were found to be better than the control in the blue scale.

Conclusion

In this study, the applicability of L-ascorbic acid, an antioxidant, as an alternative to colorments used in the leather industry was investigated. For this reason, chrome-tanned undyed crust leathers are dyed white in the finishing process. In the finishing layer, L-ascorbic acid material was added to the finishing solution at the rates of 1%, 2%, 3%, 4% and 5% L-ascorbic acid. These processes were repeated 3 times and compared with leathers treated according to the standard method without L-ascorbic acid. In these comparisons, visual evaluation, color measurement, rubbing fastness and light fastness were analyzed according to standard methods. Analysis results show that L-ascorbic acid gives the leather a pearly pink color tone while improving dry rubbing fastness and light fastness properties. For this reason, it has emerged that it can be used as a new colorment in leather finishing.

Table V

Light fastness assessment results

		Control	**Experiment**		
		n(%)	**n(%)**	**Test Value**	**p**
Blue scale	1	3 (100)	0 (0)	11.717	0.001**
	1/2	0 (0)	1 (6.7)		
	2	0 (0)	7 (46.7)		
	3	0 (0)	7 (46.7)		

Fisher Freeman Halton test **p<0.01

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Silica-Embedded Polyurea Microspheres with Rough Surface for Matte Leather Finishing

by

Liang Jia,[1] Li Wang,[1] Jing Li,[1] Jun Xiang,[1] Yi Chen[1] and Haojun Fan[1*]
[1]*Key Laboratory of Leather Chemistry and Engineering of Ministry of Education,*
Sichuan University, Chengdu 610065, China

Abstract

A type of polyurea microspheres with rough surfaces and different sizes (1-12 μm), which was used for waterborne polyurethane matte leather coating, were prepared by precipitation polymerization in H_2O/acetonitrile system, using isophorone diisocyanate as polymerized monomer, 2,4-diaminobenzenesulfonic acid sodium salt as hydrophilic monomer and nano-SiO_2 as surface roughener. The effect of the loading of isophorone diisocyanate and 2,4-diaminobenzenesulfonic acid sodium salt, the volume ratio of H_2O/acetonitrile and the addition stage of nano-SiO_2 on the particle size and surface roughness were investigated so as to achieve the excellent matte effect of the coating. The results indicated that the adding of hydrophilic monomer can reduce the particle size of microspheres and improve its re-dispersibility in water, while the increase of the proportion of acetonitrile in the mixed solvent and the loading of polymerized monomer can enlarge the size of the polyurea microspheres. As surface roughener, with the increase of nano-SiO_2 loading, the surface roughness and the particle size of microspheres increase. When nano-SiO_2 is added at the stage of the reaction system getting turbid, the maximum surface roughness of polyurea microspheres can be achieved. Polyurea microspheres with particle size (1-2 μm) and high surface roughness have better matting effect, and the gloss of the prepared waterborne polyurethane coating can be adjusted to less than 1.6° (60°-incident Angle).

Introduction

As a thin film covering the surface of the substrate, the primary functions of the coating include covering up the surface defects, protection for substrate, improving its waterproofness and so on. In addition, coating can also endow the substrate with beautiful color and various aesthetic effects.[1] With the development of aesthetic, the requirements for the color and gloss of coatings are continuously changing, the matte coatings become more and more popular[2-4] and widely used in automotive, furniture, costume and other fields.[5] According to the optical theory, a rough surface is a key issue to achieve matte effect during the coating formation. Higher surface roughness always leads to a lower surface gloss.[6] Currently, the most economical way to obtain matte coatings is by adding a variety of matte fillers into the coatings, and the matte fillers are often composed of inorganic or organic materials, such as nano-fumed SiO_2 and wax. However, the inorganic powders often cause a series of drawbacks, such as poor compatibility, worse hand feeling and low adhesion with substrate (the coating will get white by stretching).[7-9] In order to solve these problems, the research for organic matte fillers which have excellent matte effect and good affinity with waterborne polyurethane (WPU) emulsion and substrate has become a hotspot.

As a widely used organic polymer material, polyurea has excellent abrasion performance, weather durability and thermal shock resistance.[10] Furthermore, WPU has been widely used in leather/synthetic leather finishing, textile laminating, automobiles and wood coatings for its environmental friendliness and excellent comprehensive performance.[5] On account of the similarity of structure between polyurea and WPU, they should have good affinity to each other. Given a controllable size and micro-roughness surface, the microspheres themselves would have light scattering characteristics.[11,12] Meanwhile, adding different-sized microspheres into the coating can form a rough coating surface and produce matte effect.[13] The synergy of the two features is believed to give the coating superimposed matte effect.

Traditional methods for preparation of polyurea microspheres include suspension polymerization,[14] emulsion polymerization[15] and precipitation polymerization.[16] Nevertheless, the preparation of microspheres with controllable particle size and rough surfaces is still a challenge for a long time through a multiple phase system.[12] Although many works have been done to prepare microspheres with various special structures,[17] such as Walnut-like particles,[11] golf ball-like polymer particles[12] and porous microspheres[18] etc.; few studies were focused on how to control the gloss of coatings by controlling the size and morphology of particles. Meanwhile, there are few reports about the hydrophilicity of polyurea microspheres.

In this study, a series of polyurea microspheres with different sizes and surface roughness, were prepared by adjusting the loadings of 2,4-Diaminobenzenesulfonic acid sodium salt (MPDSA-Na), isophorone diisocyanate (IPDI) and surface roughener (nano-SiO_2

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*Corresponding author e-mail: fanhaojun@scu.edu.cn
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powder), the volume ratio of acetonitrile (AN) and H_2O, and the addition stage of nano-SiO_2. Meanwhile, the influence of particle size and surface of microspheres on the matte effect of WPU coating were investigated.

Experimental

Materials

IPDI was acquired from Dymatic Post Polymer Material Co. (Lishui, China). MPDSA-Na and nano-SiO_2 were obtained from Aladdin. The AN solvent was supplied by Kelong Chemical Engineering Co. Ltd (Chengdu, China). WPU(35% solid content) was obtained from Lanxess Co. All chemicals were used as received unless stated otherwise.

Preparation of polyurea microspheres with different surface roughness[19]

Preparation of polyurea microspheres with smooth surface: Figure 1 shows the reaction steps of IPDI. H_2O/AN mixture (100g, 1/4, 3/7, 2/3) was first charged into the reaction bottle, followed by addition of IPDI (1 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt%), and MPDSA-Na (6 wt%, 10 wt%, 14 wt% and 18 wt% of the IPDI). The bottle was sealed off, hand-shaken to make the mixture homogeneous, and left standing still (without any oscillation or stirring) in a water bath at 50°C for 5 hours.

Preparation of polyurea microspheres with rough surface: Nano-SiO_2 was used as surface roughener. IPDI, MPDSA-Na and nano-SiO_2 (0 wt%, 60 wt%, 80 wt% and 100 wt% of the IPDI) were dissolved in H_2O/AN solution to form a homogenous solution. The bottle was sealed off, and the precipitation polymerization was carried out in a water bath for 3 h at 50°C under oscillation.

Samples were centrifuged for 5 min at 4000 rpm. Then the precipitate was filtered and washed with deionized water for 5 times so as to remove the unreacted hydrophilic monomer MPDSA-Na and other water-soluble impurities. Finally, the precipitate was dried for 6 h at 80°C and the microspheres were obtained.

Preparation of WPU matte coating[13]

The polyurea/WPU composite was prepared by adding 5 wt% polyurea microspheres (based on WPU emulsion), small amount of flowing agent (1.6 wt%) and thickening agent (1 wt%) into WPU. The mixture was stirred in a beaker at 500 rpm until the viscosity reached 1000 mPa.s, and then coated it on the synthetic leather and natural leather surface with a drying process at 120°C for 3–5 minutes.

Characterization

The element and structure of the polyurea microspheres were analyzed by X-ray photoelectron spectroscopy(XPS) and Fourier infrared spectrometer(FTIR). And the morphology of microspheres was observed by scanning electron microscope (SEM, JSM-7500F, Japan). Size (Dn) and size distribution (Dw/Dn) were calculated by counting about 200 microspheres on the SEM pictures.[20] Re-dispersibility was tested by adding the polyurea microspheres into deionized water to observe the sedimentation velocity of the microspheres.[21,22] Glossmeter (REFO 60, Germany) was used for measurement of surface gloss with a 60°-incident angle. Each sample was tested five times on different districts and its average data was reported.

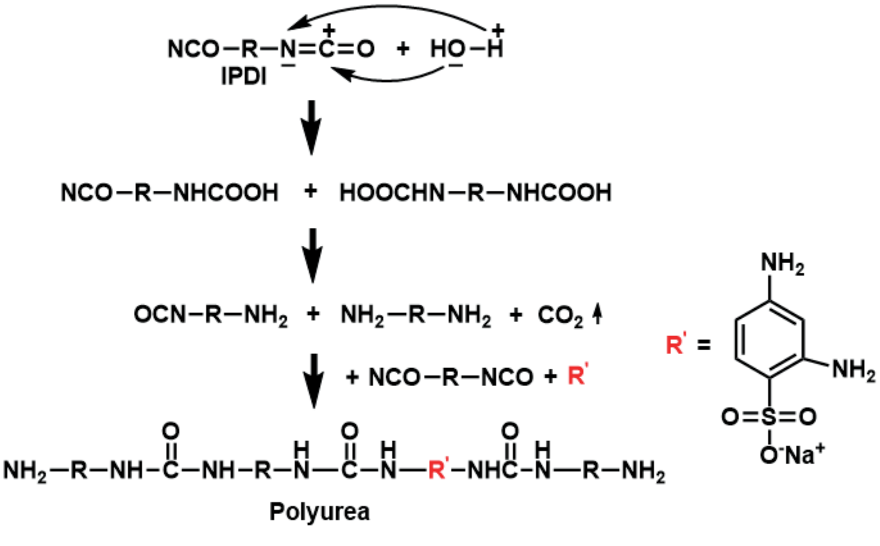

Figure 1. The reaction steps of IPDI

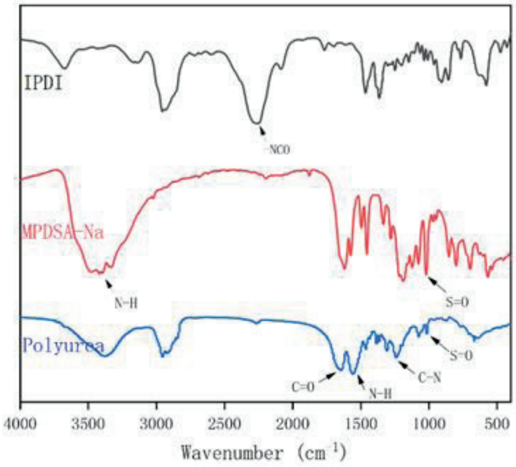

Figure 2. The FTIR spectra of polyurea microspheres

Results and discussion

Structural of polyurea microspheres

IPDI, MPDSA-Na and purified polyurea microspheres with smooth surface were analyzed by FTIR and XPS respectively. In FTRR of IPDI in Figure 2, the absorption peak at 2264 cm^{-1} confirmed the -NCO stretching vibration, after polymerization, this peak disappeared. In FTIR of hydrophilic monomer MPDSA-Na, the peak at 3419 cm^{-1}, 1190 cm^{-1} respond to the N-H stretching vibration and the S=O stretching vibration in the sulfonic acid group. Correspondingly, these peaks occurred in the FTIR of the polyurea microsphere at 3379 cm^{-1} (ascribed to the N-H stretching vibration in -NHCONH-) and 1190 cm^{-1} (assigned to the stretching vibration of S=O in sulfonic acid group) separately,[16] which indicate that the hydrophilic group was successfully grafted to the surface of the polyurea microspheres. In Figure 3 of XPS analysis, the binding energy at 167.2eV referred to the characteristic peak of S2p, which was identified as the characteristic peak of S element in the sulfonic acid group.[23] Combined with FTIR and XPS analysis, it was shown that the MPDSA-Na had reacted with IPDI and the sulfonic acid group was introduced to the surface of polyurea microspheres.

Influence of MPDSA-Na loading on microsphere size and its re-dispersibility

As a matte filler for WPU coating, polyurea microspheres should have re-dispersibility in water. But the polyurea microspheres are hard to be re-dispersible in WPU due to its-hydrophobicity.[24] To solve this problem, hydrophilic monomer MPDSA-Na is used to improve their hydrophilicity and re-dispersibility. Figure 4 shows the size and dispersion of the polyurea microspheres with 6 wt%, 10 wt%, 14 wt% and 18 wt% MPDSA-Na loadings (based on IPDI, respectively). As can be seen that polyurea microspheres with 6 wt%-10 wt% MPDSA-Na loadings show larger size and good dispersion, whilst with 18 wt% MPDSA-Na shows uneven size and poor dispersibility, for 18 wt% loading, some microspheres even appeared agglomerated. The results indicated that the high an amount of MPDSA-Na was not conducive to obtain polyurea microspheres with good dispersion. Table I lists the particle size variation of polyurea microspheres with the MPDSA-Na loading. When the loading increased from 6 wt% to 18 wt%, the particle size of polyurea microspheres decreased from 9.31 μm to 6.04 μm, showing a decreasing trend. The reason could be ascribed to the enhanced charge density, which prevents primitive particles from approaching and fusing with each other to form large-size microspheres.[13] The best loading is 14 wt% for that the microspheres have better hydrophilicity and not agglomerate like Figure 4d.

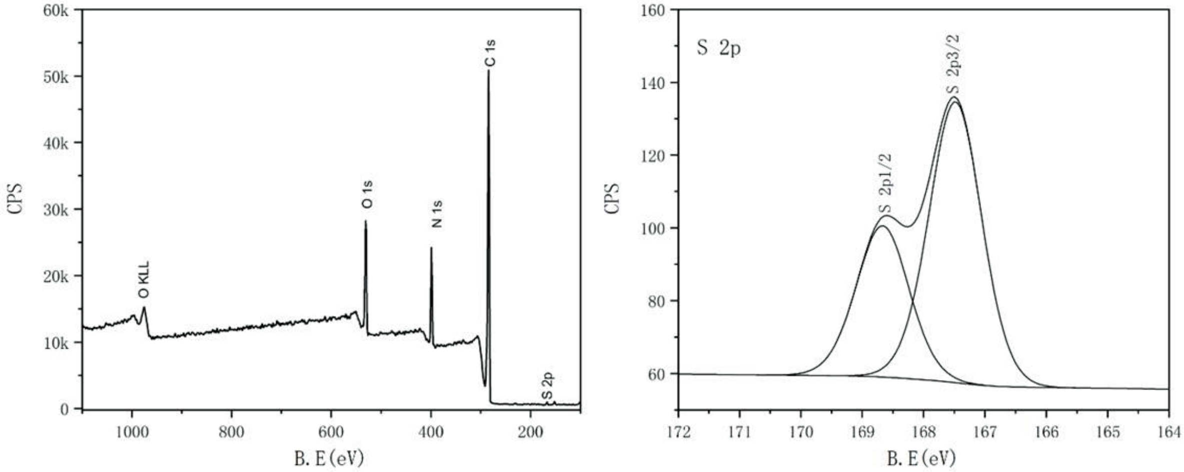

Figure 3. The XPS analysis of polyurea microspheres

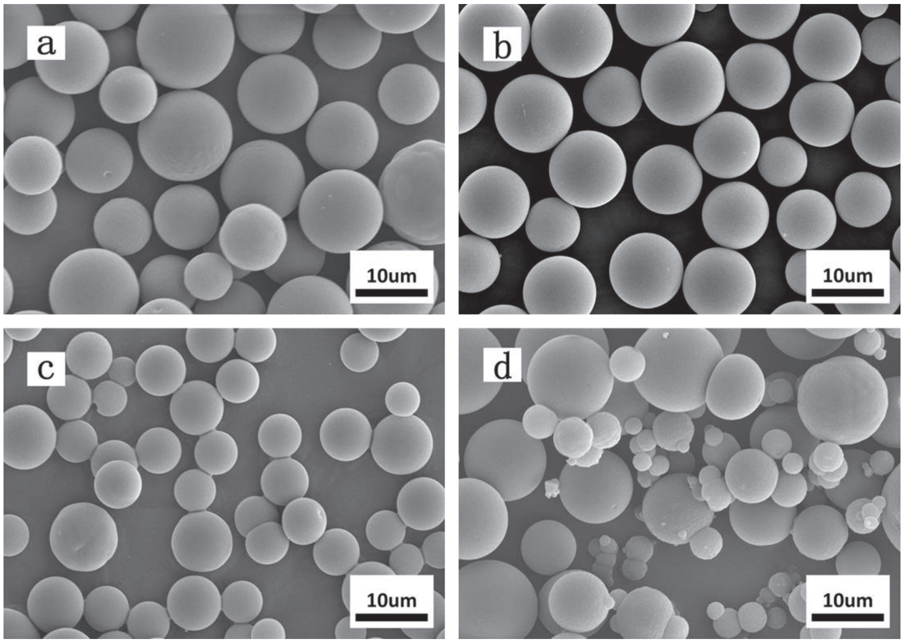

Figure 4. The effect of MPDSA-Na loading (wt%) on polyurea microsphere size:
(a) 6; **(b)** 10; **(c)** 14;**(d)** 18.

Table I

D_n and D_n/D_w of polyurea microspheres at different MPDSA-Na loading

	MPDSA-Na loading (wt%)	D_n/μm	D_w/μm	D_n/ D_w
a	6	9.31	11.59	1.24
b	10	8.66	9.92	1.15
c	14	6.83	7.81	1.14
d	18	6.04	12.06	1.99

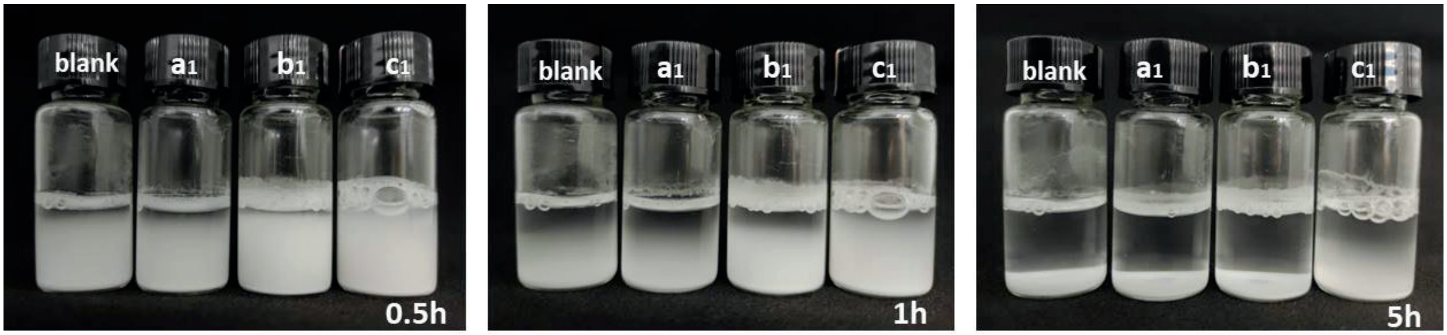

Figure 5. The dispersion stability of polyurea microspheres understanding for different periods

Table II

D_n and D_n/D_w of polyurea microspheres at different H_2O/AN

	H_2O/AN	D_n/μm	D_w/μm	D_n/ D_w
a	2/3	5.38	6.49	1.21
b	3/7	6.83	7.81	1.14
c	1/4	8.82	11.53	1.31

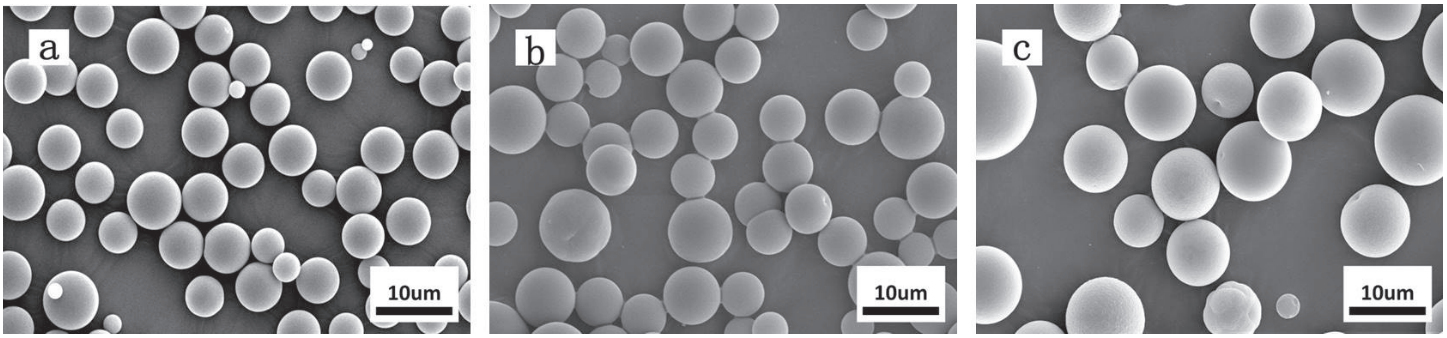

Figure 6. The effect of H_2O/AN on polyurea microsphere size: **(a)** 2/3; **(b)** 3/7; **(c)** 1/4

The polyurea microspheres without hydrophilic groups (blank) and the polyurea microspheres a, b and c mentioned in Figure 2 were added to the deionized water to form 2 wt% dispersion solution and named blank, a_1, b_1 and c_1 respectively (Figure 5). The polyurea microsphere dispersion was left standing at room temperature and photographed after 0.5 h, 1 h and 5 h to observe their dispersion state. It can be seen that after 0.5 h of standing, stratification began to occur in a_1, b_1 and blank. After standing for 1 h, c_1 also began to stratify. After standing for 5 h, the microspheres in a_1, b_1 and blank were completely precipitated, while those in c_1 were not completely precipitated. The results show that increasing the loading of hydrophilic monomer can improve the dispersion stability of the microspheres in water.

Influence of H_2O/AN volume ratio on microsphere size

Volume ratio of H_2O/AN can change the polarity of the mixed solvent. Higher proportion of AN in the solvent will increase the solubility of IPDI and its oligomer. In addition, water in the solvent also participates in the reaction, its amount imposes an obvious effect on the particle nucleation.[19] Therefore, solvent volume ratio has an important effect on the size of microspheres. Figure 6 shows the size variation of polyurea microspheres in different H_2O/AN volume ratio (2/3, 3/7, 1/4, respectively). The corresponding size of the microspheres obviously enlarged from 5.38 μm to 8.82 μm with AN content in the mixed solvent increased from 60% to 80% (Table II). The increasing trend is attributed to the increased solubility of the oligomers in the solvent. At the same time, narrower size distribution was obtained for the runs with H_2O/AN volume ratio at 3/7, while the uniformity of microspheres deteriorated with enlarged size distribution (H_2O/AN volume ratio at 2/3 and 1/4). It can be argued that polymerization in the binary solvent with a low AN amount creates a huge number of primitive particles, leading to their partial or limited aggregation during the process; whereas polymerization in the solvent with a higher AN content postpones particle aggregation, resulting in an extended and continuous nucleation. Both of the two circumstances will cause a broadened size distribution for the microspheres.

Influence of IPDI loading on microsphere size

On account of that high IPDI loading in the binary solvent can create a huge number of primitive particles, the amount of it has an important effect on the size of the microspheres in precipitation polymerization.[22,25]

Figure 7 shows the size of polyurea microspheres prepared with different IPDI loading (1 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt%, respectively). When the IPDI loading was increased from 1 wt% to 10 wt%, the microspheres did not agglomerate and could form independent microspheres with good dispersion. As shown in Table III, the particle size of microspheres enlarged from 2.55 μm to 11.48 μm with the increase of the IPDI amount from 1 wt% to 10 wt%. Generally, the increase of the IPDI loading can enhance the concentration of primitive particles, and the collision probability among primitive particles will increase. Therefore, there are more small particles fused to form large particles. Besides, the D_n/D_w of microspheres are found to be related to the IPDI loading, when the IPDI loading is 1 wt% and 4 wt%, the D_n/D_w of microspheres are 1.01 and 1.02 and are close to highly uniform size.[25] When

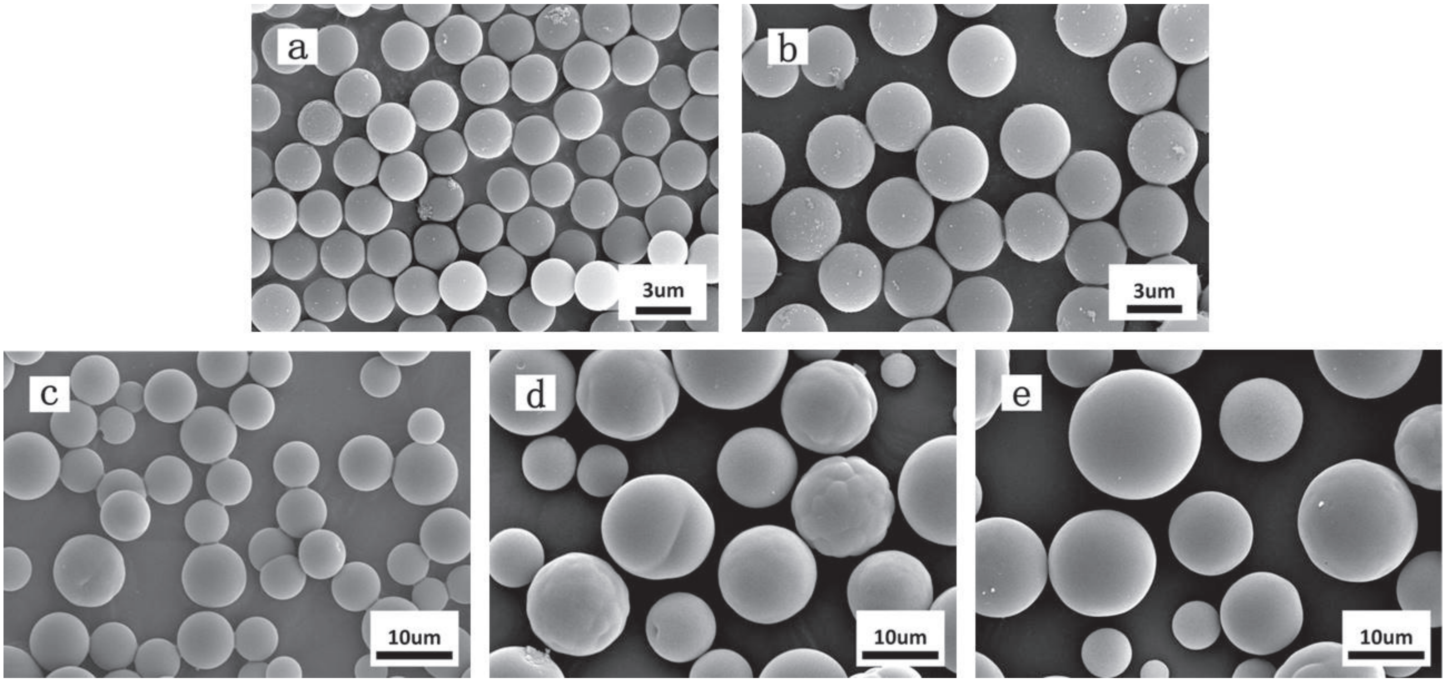

Figure 7. The effect of IPDI loading (wt%) on polyurea microsphere size: **(a)** 1; **(b)** 4; **(c)** 6; **(d)** 8; **(e)** 10

Table III
Dn and Dn/Dw of polyurea microspheres at different IPDI loading

	IPDI loading (wt%)	D_n/μm	D_w/μm	D_n/ D_w
a	1	2.55	2.57	1.01
b	4	3.56	3.62	1.02
c	6	6.83	7.81	1.14
d	8	10.70	12.94	1.21
e	10	11.48	14.56	1.28

the IPDI loading is above 4 wt%, the size microspheres exhibited polydispersity. This is highly possible because there are still many primitive particles in the binary solvent when large-size microspheres formed in the system, which leads to the increase of D_n/D_w.

In terms of matte coating, it is noted that the larger the size of the microsphere, the worse the matte effect appeared. When the microspheres are large enough to form a smooth surface for themselves, they cannot scatter the incident light, so good matting effect cannot be achieved. That is, even if the size and dispersity of the polyurea microspheres are well controlled, the microspheres with smooth surface could not give the coating ideal matting effect.

Effect of nano-SiO_2 loading on surface roughness of polyurea microspheres

In order to increase the light scattering characteristics of the surface, nano-SiO_2 was used as surface roughener to create the roughness on the surface of microspheres. Figure 8 shows the surface roughness of polyurea microspheres with different nano-SiO_2 loadings (0 wt%, 60 wt%, 80 wt% and 100 wt% of the IPDI, respectively). As can be seen from Figure 8, the polyurea microspheres with different nano-SiO_2 loadings did not agglomerate but formed independent microspheres with good dispersity. Most importantly, all polyurea microspheres exhibited a rough surface with the addition of nano-SiO_2. Compared with the control sample (3.56μm) without nano-SiO_2 in Figure 8 and Table IV, the particle size of other microspheres enlarged from 5.93 μm to 9.26 μm with the increase of nano-SiO_2 loading from

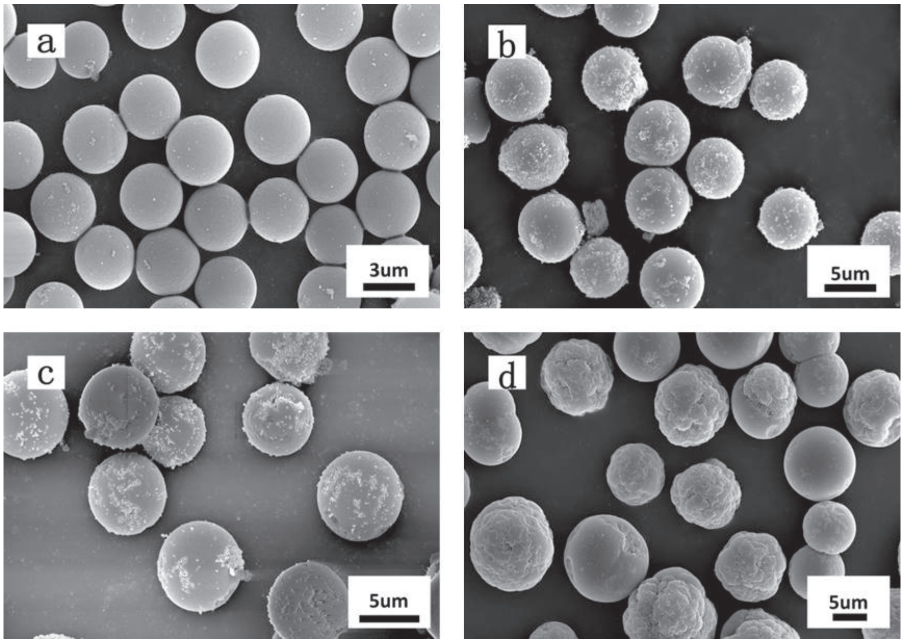

Figure 8. The effect of nano-SiO_2 loading (wt %) on polyurea microsphere size and morphology: **(a)** 0; **(b)** 60; **(c)** 80; **(d)** 100.

Table IV

D_n and D_n/D_w of polyurea microspheres at different nano-SiO_2 loading

	SiO_2 loading (wt %)	**D_n/μm**	**D_w/μm**	**D_n/ D_w**
a	0	3.56	3.62	1.02
b	60	5.93	6.07	1.02
c	80	6.58	6.77	1.03
d	100	9.26	9.84	1.06

60 wt% to 100 wt%, the reason could be that nano-SiO_2 enters the microsphere core and increases the microsphere size.

Influence of nano-SiO_2 addition stage on surface roughness of polyurea microspheres

Figure 8 shows that increasing the amount of nano-SiO_2 could only improve the surface roughness of polyurea microspheres to a certain extent. Further analysis theorized that a large amount of nano-SiO_2 could be wrapped in the interior of polyurea microspheres, leading to the surface of the polyurea microspheres not being so rough. So, the addition stage of nano-SiO_2 was changed to confirm the above theory. Figure 9 shows the surface morphologies of polyurea microspheres prepared by adding nano-SiO_2 at different stages (at the beginning of the reaction, at the stage of the reaction system getting turbid, and half an hour after the reaction system getting turbid). As can be seen from Figure 9, the relative surface roughness of polyurea microspheres is greater for nano-SiO_2 added at the stage of the reaction system getting turbid than for others. When the nano-SiO_2 was added at the beginning of the reaction, a large loading of nano-SiO_2 was wrapped inside the polyurea microspheres during the reaction process, resulting in low surface roughness of the microspheres. When the nano-SiO_2 was added half an hour after the reaction system began increasing in turbidity, plenty of nano-SiO_2 particles were adsorbed on the surface of the microspheres and the space between them thus, no rough surfaces were formed. When the nano-SiO_2 was added at the stage of the reaction system becoming turbid, a large number of particles grew to be insoluble in mixed solvents and began to precipitate, in this case, the added nano-SiO_2 was embedded on the surface of polyurea microspheres during the precipitation process, thus embedded nano-SiO_2 particles give the microspheres the maximum surface roughness (Figure 9b).

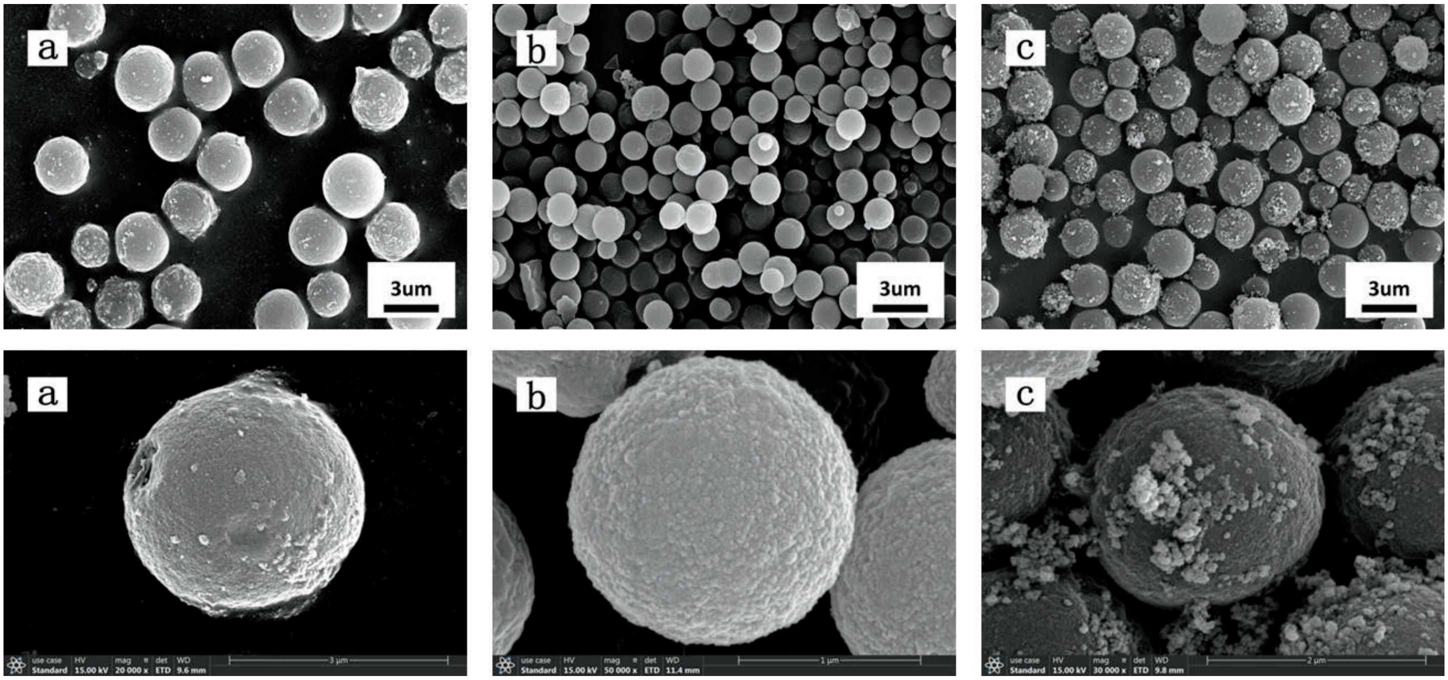

Figure 9. The effect of adding nano-SiO_2 at different stages on polyurea microsphere size and morphology: **(a)** at the beginning of the reaction; **(b)** at the stage of the reaction getting turbid; **(c)** half an hour after the reaction getting turbid

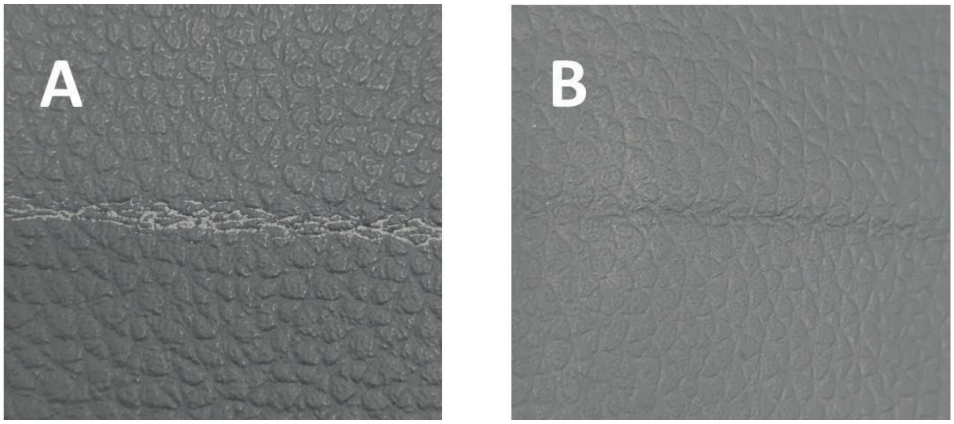

Figure 10. The digital photos of surface coated with: **(A)** SiO_2-embedded matteing powder; **(B)** polyurea microspheres

Table V

The polyurea microspheres with different sizes and size distribution

sample	D_n/μm	D_n/ D_w	SEM images
a	11.48	1.28	Fig. 7 e
b	9.31	1.24	Fig. 4 a
c	6.83	1.14	Fig. 4 c
d	9.26	1.06	Fig. 8 d
e	2.90	1.04	Fig. 9 a
f	1.49	1.07	Fig. 9 b

Influence of different polyurea microspheres on the gloss of WPU coating

Just as mentioned above, the addition of inorganic matting powder usually results in the decrease of adhesion of the coating, and the coating often gets white after stretching and hot pressing. Figure 10 shows the comparison of coatings with added SiO_2 matte powder and polyurea microspheres. The sample shown in Figure 10-A (coated with SiO_2-embedded matte powder) obviously becomes white after folding, while the one shown in Figure 10-B (coated with polyurea microspheres) does not become white after stretching and folding, which reveals that the coating with polyurea microspheres has no negative effect on adhesion.

The influence of different polyurea microspheres on the gloss of WPU coating was studied, and the particle size and surface morphology of these microspheres were listed in Table V.

Figure 11 shows the gloss of the corresponding synthetic leather coating with different microspheres listed in Table V. It can be seen that the gloss of blank coating without adding polyurea microspheres is 5.73° and the gloss of other coatings decreased to 1.27°-2.9° after adding 5 wt% polyurea microspheres in WPU, indicating that all microspheres have an ability to reduce the coating's gloss. When the particle size of the polyurea microspheres with smooth surface decreased from 11.48 μm to 2.55 μm, the corresponding gloss of the coating decreased from 2.9° to 2.03°, indicating that small particle size contributes better matting effect. Similarly, when the particle size of the polyurea microspheres with rough surface decreased from 9.26 μm to 1.49 μm, the gloss of the corresponding coating decreased from 2.4° to 1.57°. This indicates that small particle size and rough surface impart the coating higher matting effect. Comparing with the microspheres (b) and (d) with similar particle size (9.31 μm and 9.26 μm) but different surface roughness the gloss of corresponded coating are 2.4° (b_1) and 2.77° (d_1), also indicating the microspheres with rough surface show higher matting characteristics. The microspheres (d) keep good consistency with our experimental expectation.

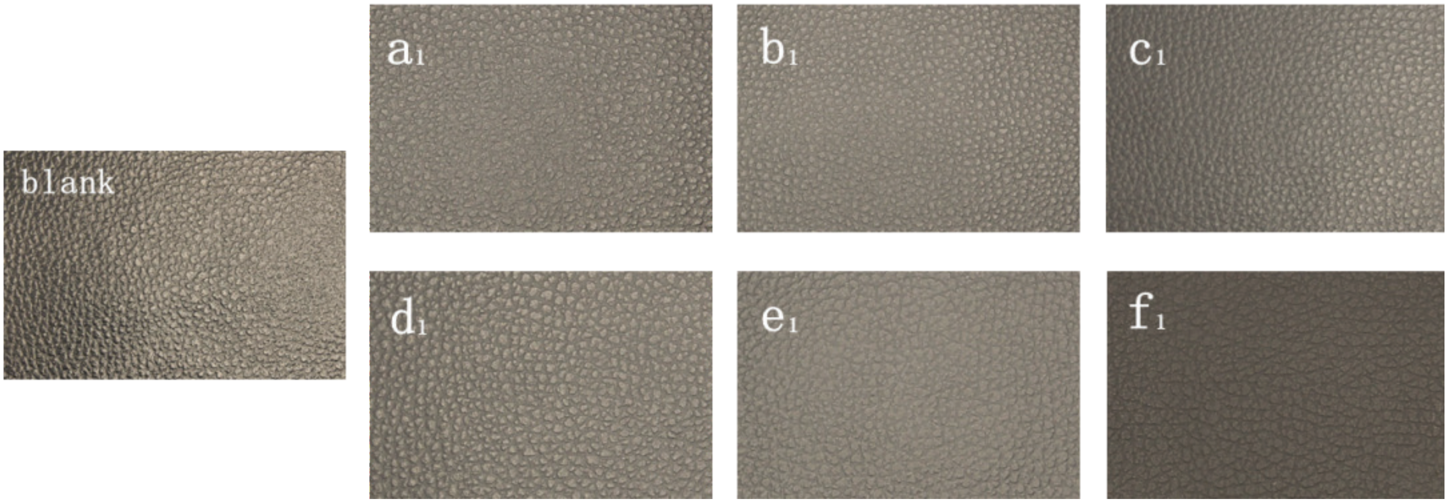

Figure 11. The digital photos of coating surface with different types of polyurea microspheres (listed in table V)

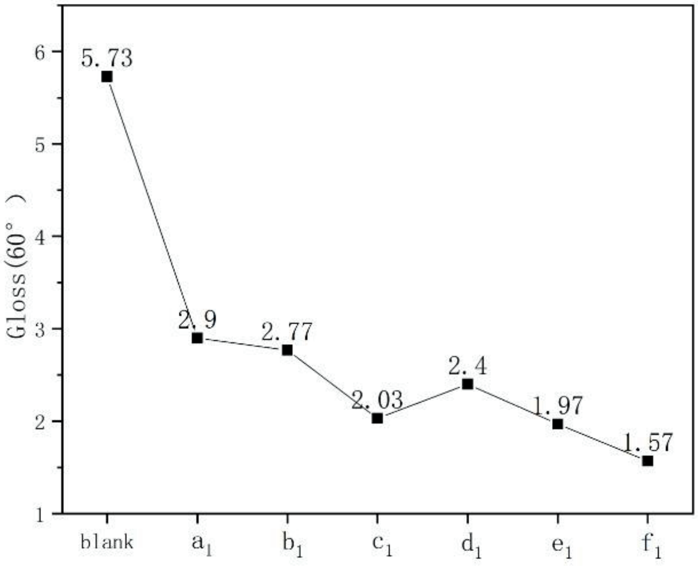

Figure 12. Glossiness of the corresponding coating in Figure 11

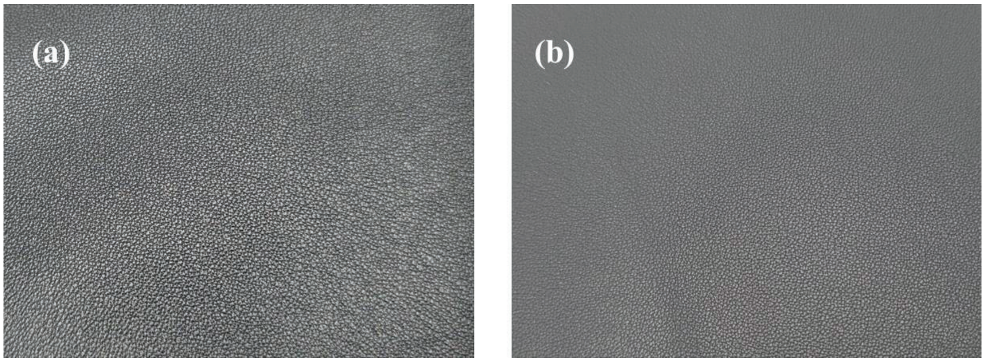

Figure 13. The digital photos of natural leather with different coating surface: **(a)** blank coating; **(b)** coating containing rough surfaced polyurea microspheres

Figure 13 shows the gloss of the natural leather coating with and without rough surfaced polyurea microspheres. The gloss of Figure 13 (a) is 3.90, and the gloss of Figure 13 (b) is 1.53. The results indicate that the coating containing rough surfaced polyurea microspheres also has excellent matting effect on the natural leather.

Conclusion

Polyurea microspheres with different sizes and surface roughness were prepared by precipitation polymerization in H_2O/AN system. And the effects of the loading of MPDSA-Na and IPDI, the volume ratio of H_2O/AN and the addition stage of nano-SiO_2 on the size and surface roughness of microspheres were investigated in detail. Furthermore, the effects of different polyurea microspheres on the gloss of WPU coating were also investigated. The results show that the re-dispersibility of as-prepared microspheres in water can be ensured with 14 wt% MPDSA-Na. The size and size distribution of the microspheres can be controlled by the loading of IPDI, MPDSA-Na, nano-SiO_2 and the volume ratio of H_2O/AN, whilst the surface roughness of the microspheres strongly relies on the addition stage of nano-SiO_2. Under the optimized condition of 1 wt% IPDI(based on solvent), 14 wt% MPDSA-Na (based on IPDI), 80 wt% nano-SiO_2 (based on IPDI), 3:7 H_2O/AN volume ratio and 50°C reaction temperature, the size of polyurea microspheres can be controlled in a range of 1.49 μm to 2.9 μm with monodispersity and higher rough surface. When 5 wt% microspheres are mixed with WPU for leather coating, no negative effect on adhesion is observed. Finally, the polyurea microspheres with particle size between 1-2μm and high surface roughness imparted the coating excellent matting effect, and the gloss of the resultant leather coating can be decreased from 5.73° to less than 1.6°.

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Authors' contributions

Liang Jia: Conceptualization, Methodology, Formal analysis, Writing - Original Draft, Jing Li: Data curation, Formal analysis, Li Wang: Validation, Investigation, Yi Chen: Visualization, Jun Xiang: Writing- Reviewing and Editing, Validation, Jun Yan: Validation, Haojun Fan: Writing - Review & Editing, Supervision.

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Availability of data and materials

All data generated or analyzed during this study are included in this article.

Declarations

Competing interests

The authors declare no competing interest.

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Manufacture of Exotic Leather and Small Leather Goods from Ovine Stomach

by
Peris N. Wainaina,[1] Benson Ongarora[2] and Paul Tanui[2]
[1]*Kenya Leather Development Council,* Nairobi, Kenya
[2]*Department of Chemistry, Dedan Kimathi University of Technology*, Private Bag, Dedan Kimathi - Nyeri, Kenya

Abstract

Leathers made from exotic skins or rare parts of animals have very good market value. The exotic leathers are usually preferred because of their patterns, naturally occurring marks and their unique structures. The objective of this study was to investigate the feasibility of tanning the ovine stomach into novelty leather and leather products. The ovine stomach was converted into an exotic leather using oil tanning methodology, with goat oil as a tanning agent. The rumen and reticulum parts of the stomach were taken through pre-tanning, tanning and post-tanning operation. The resultant leather had a different grain from the ordinary leather. Then mechanical operations like drying, toggling and staking were done. Physical properties of the leathers were analyzed by determining their thickness, tensile strength, elongation at break, tear strength, flex endurance and ball burst extension test. The grain structure of the leathers was analyzed using a light microscope. The results of physical tests were poor compared to the grains of conventional leathers since the composition of raw outer coverings of animals and those of the stomach are different. The leather processed from this non-conventional source has been found suitable for manufacturing fancy small leather goods like coin purse, key holders, purses and wallets.

Introduction

Exotic leather production refers to the tanning of the outer covering of rare species of animals and other parts of animals that are not used for making leather.[1] The beauty, durability, texture, and extraordinary properties of these leathers have fascinated many people. Several types of skins such as crocodile, ostrich, emu, alligator,[2] stingray, eel, snake, shark,[3] pythons, frogs,[4] lizards and stingray fish[5] have become popular as materials for making leather for fashion apparel, footwear, accessories, and interior products.[6] The use of exotic skins dates back to the early man. The hunting and the gathering communities used skins from reptiles, birds, fish and amphibians for adornment to their clothing or for their head-dresses as well as for covering articles such as drums.[7] The skins were made less resistant to putrefaction by drying, they were made supple by fleshing and applying animal oils.[7] Different animals have different features that provide leather with varying properties and these have resulted in increased demand for various leather products in the market.[6]

There are four compartments of the stomach of a ruminant animal. These are the abomasum, omasum, rumen and reticulum. The abomasum is the main diction and absorption compartment of the stomach. Rumen, the bulk of the stomach, constantly mixes, turns and digests the food.[8] The inside of the rumen is lined with finger like structures called papillae.[1] The papillae help to increase digestion by moving the food around inside the rumen. The omasum is made up of many folds. The reticulum looks like a honeycomb.[8] The reticulum differs from the rumen regarding to the texture of its lining. The reticulum is lined with ridges that form a hexagonal honeycomb pattern. Despite the differences in the texture of the lining of the two parts of the reticulorumen, it represents one functional space.[9]

The process of converting raw material into exotic leather generally involves three steps, with the first step being pre-tanning. Pre-tanning involves soaking, liming and unhairing, deliming, bating, pickling and degreasing to remove unwanted components, hair, adipose tissue, fats, etc., leaving a network of fiber proteins.[10] The next step, tanning, involves reacting the pre-tanned material with suitable tanning agents such as chrome, vegetable, combined tanning or oil to produce a stabilized fiber structure.[11] Finally, post-tanning which involves neutralization, retanning, dyeing, fatliquoring and finishing in order to improve fiber characteristics and to produce a useful product.[12] In the present study the rumen and the reticulum parts of the stomach were processed into exotic leather with a grain, which has a different variety from the ordinary leather.

Experimental procedures

Sample collection and preparation

The ovine stomachs were collected from a slaughter house in Nyeri town, Kenya. The stomachs were cleaned by washing dirt with clean water and cutting off the unwanted parts on the stomach. Goat oil was obtained using the procedure described in literature.[13]

Pre-tanning

The ovine stomachs were washed using 400% water and 0.5% wetting agent. The stomachs were washed thoroughly and drained until

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*Corresponding author email: periswayne@gmail.com
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they were clean. Liming was done with 200% water and 8% lime (in two portions) for 24 hours, with the drum left to stand for every 15 minutes for every two hours. The tanning drum was drained and the limed pelts were washed with clean water. During deliming process, 150% water at normal temperature, 2% ammonium sulphate and 1% sodium metabisulfate were added and the drum left to run for one hour. The cross-section was checked by phenolphthalein (colorless). The delimed stomachs were then bated with 1% enzymatic bate for one hour.

Tanning

Tanning of the ovine stomach was carried out according to the recipe provided in Table I.[13] Goat oil tannage was conducted since we had reported in our previous work that cod oil had poor rating in terms of odor compared to goat oil. The resultant leather was then dyed, horsed up, dried and staked.

Leather analysis

The leather was conditioned using ISO 2419 test method. Physical and organoleptic properties of leather were tested.[14] Physical properties, which included thickness, tensile strength, elongation at break, tear strength, flex endurance and ball burst extension test were measured using IUP methods. Organoleptic properties, i.e., softness, color and grain pattern, and general appearance were tested by leather experts. Sink test and Eward effect were also conducted.

Structural analysis

The grain patterns of the exotic chamois leather from the reticulum and rumen stomach were analyzed using a Light Microscope, Zeiss Axio Zoom.V16. The samples were analyzed by cutting pieces measuring10 mm by 10 mm, clamping them on the stage and the micrographs for the grain pattern was obtained by operating the microscope at (16×) magnification.

Results and Discussion

Sink test

When the stomach chamois leather was immersed in cold water, it absorbed little amount of water. This could be because the amount of water absorbed depend greatly on the porosity of the hide or skin, thus indicating that oil tanned stomach is not very porous.[15] The leathers were buffed on flesh side with the aim of improving water absorption capacity of the leather but no appreciable increase in the amount of water absorption was noted. It was also observed that buffing and snuffing on either side of the stomach leather was not effective.

Eward effect

Ovine stomach chamois leather showed unique Eward effect, whereby when immersed in hot water at about 70°C, they shrunk immediately and the area became thick and when the shrunken leathers were immersed in cold water, they relaxed immediately and regained 90% of its original area implying that the leathers passed the Eward effect test. Oil-tanned leather is one of a few cases where the leather exhibits reversibility effect following hydrothermal shrinking.[16]

Table I

Recipe for oil tanning of the ovine stomach

Process	Chemicals	Amount (%)	Time (h)	Remarks
Pickling	Water Salt Formic acid Sulfuric acid	150 10 0.8 1	2	The pH was adjusted to 3.2
Pre-tanning	Glutaraldehyde	0.5	2	The pH was adjusted to 8.5 and the skins were piled for 12 hours
Oil tanning	Oil (Goat oil)	30	6	The skin was uniformly drummed along with oil for 6 hours
Oxidation (inside the drum)	Hydrogen peroxide	6	4	The skin was drummed for 4 hours
Oxidation (outside the drum)			12	The materials were hung on the toggle drier at room temperature
Alkali wash	Water Soda ash Wetting agent	400 0.25 0.5	1	The leather was washed three times and drained.

Table II

Physical properties of ovine stomach leather

Physical properties		**Exotic chamois leather** **Reticulum stomach leather**	**Rumen stomach leather**	**Standard value SNI06-1752-1990 (minimum)**
Thickness (mm)		1.22 ± 0.19	0.65 ± 0.12	0.3 - 1.5
Tensile strength (N/mm^2)		15.64 ± 0.86	11.51 ± 0.61	>7.5
Elongation at break (%)		58.63 ± 1.24	45.01 ± 1.22	>50
Tearing strength (N/mm)		33.01 ± 0.51	28.90 ± 0.61	>15
Flex endurance at 100,000 flexes		No damage	No damage	No damage
Ball burst extension (mm)	Grain crack	7.79 ± 0.21	5.88 ± 0.22	6.5
	Grain burst	8.45 ± 0.22	6.93 ± 0.06	7

Physical tests

The physical properties of the chamois leathers obtained thus are summarized in Table II below.

Thickness

The oil tannage, which is actually a "shrinkage" tannage, raised the thickness of ovine stomach. From the results recorded in Table II, it could be observed that the thickness of reticulum and rumen part of the stomach leather was 1.22 ± 0.19 mm and 0.65 ± 0.12 mm respectively. These thicknesses achieved by the exotic chamois leather were within the minimum recommended values.[17]

Tensile strength

Tensile strength of leather is the greatest longitudinal stress leather can bear without tearing apart. The tensile strength of leather is determined by the fibrous structures that constitute the collagen network structure and the modification of this structure by the tanning agents.[16] The minimum tensile strength for chamois leather should be at least 7.5 N/mm^2.[17] This study found the tensile strength of the exotic chamois leather was higher than 7.5 N/mm^2. The reticulum part of the exotic leather had a tensile strength of 15.64 ± 0.86 N/mm^2 while the rumen part had a tensile strength of 11.51 ± 0.61 N/mm^2. Leather obtained from the rumen recorded lower tensile strength as compared to the tensile strength of the reticulum part and this could be attributed to the fact that leather is anisotropic in nature.[18] The hexagonal honeycomb-like structures on the reticulum may also be playing a role as a reinforcement of the belt, thus making it less susceptible break compared to the rumen.

Elongation at break

Elongation refers to the ability of a leather product to lengthen/stretch when stress is applied to it and represents the maximum extent leather can stretch without breaking. Elongation is an important property to be considered when choosing leathers because a low elongation value results in easy tear while a high elongation value causes leather goods to be deformed very quickly or even lose usability.[19] Leathers that have a lower tensile strength have a lower percentage elongation and vice versa. From Table II, it could be observed that the percentage elongation of reticulum and rumen part of the stomach leather was 58.63 ± 1.24 and 45.01 ± 1.22 respectively. The elongation at break of the rumen was poor since it was below the minimum recommended value while the elongation at break of the reticulum part of exotic chamois leather met the standard of 50% minimum.[17] The observed trend could as well be attributed to the honeycomb-like features on the surface of the reticulum.

Tearing strength

The strength of the leather products in use is indicated by the quality standard relating to tearing load. Table II shows that all the leathers tested had more than 15 N/mm which is the minimum recommended value of tear strength of chamois leather and it was concluded that the leather fulfilled the SNI-06-1752-1990 standard.[17] The tearing strength of the rumen part of the leather recorded lower tearing strength as compared to the reticulum and this could be attributed to different parts of the stomach serving different purposes and therefore having different properties.[18] Similarly, the characteristic patterns on the surfaces of the different parts of the stomach could be at play as pointed out earlier.

Flexing endurance

Flexing test was applied to the respective leathers and there was no damage at 100,000 flexes to any of the leathers. All the studied leather samples passed the flexing test hence, it could be inferred that the method of tanning did not affect the flexing endurance of the leathers. Therefore, the obtained exotic leathers could be used to make small leather product that flex.

Ball burst test

The ball burst test is another physical property for testing quality of leathers. It is intended to indicate the grain resistance to cracking.

Figure 1. Photographic plate of finished ovine stomach chamois leather

From Table II, it could be observed that the reticulum part of chamois leather samples tested had values 7.79 ± 0.21 mm, 8.45 ± 0.22 mm for grain burst and grain crack respectively, which are higher than the minimum recommended values of 6.5 mm and 7.0 mm. The rumen part failed the test since it recorded lower values of 5.88 ± 0.22 mm and 6.93 ± 0.06 mm respectively for grain crack and gain burst against the above minimum recommended values.[17] Pre-tanning, tanning and post tanning processes and also the type of raw material are known to affect the grain crack and grain burst test.[20] Howbeit, in this case, it is evident from Table II that the thickness also affected all the analyzed physical properties. The rumen that recorded lower thickness value consistently displayed lower values in all the conducted tests.

Color and dyeing

The stomach leathers were yellow except for papillae which were light brown. According to the SNI 06-1752-1990, preferred color of chamois leather is yellow to nearly white.[17] The color possibly indicates that oxidation on the papillae was faster and more severe than on the stomach, and a brown color in oil tanning always point to a fast rate of auto oxidation.[15] Due to poor color uniformity of the exotic chamois leather, the leathers were dyed and this gave uniform color to the leathers as shown in Figure 1 below. The color intensity of the applied dye ranged between 6-7 as shown in Table III.

Organoleptic properties

The table below shows the organoleptic properties of the exotic leathers from ovine stomach.

Table III
Organoleptic properties of stomach leather

Organoleptic properties	Reticulum leather	Rumen Leather
Softness	6	7
Color intensity	7	6
General appearance	8	8
Grain pattern	9	8

The evaluated organoleptic properties of the chamois leather included softness, color intensity, general appearance and grain pattern. Soft leather tends to increase its water absorption and flexibility, so it will provide comfort during use[15]. From Table III, it can be seen that organoleptic properties of the leathers obtained from this study were above average on a scale of 10. Color intensity of the stomach leathers ranged between 6-7. This shows that the dye had penetrated. The obtained leather had unique appearance which was different from the ordinary leather. Reticulum leather was lined with ridges that form hexagonal honeycomb-like patterns while rumen leather was covered in small finger-like projections called papillae, which are flattened. These features gave the leathers an appealing look (given the general appearance rating of 8) as shown in Table III.

Grain structure

The grain structures of the leathers obtained from reticulum and rumen parts of the stomach are shown in Figure 2. The reticulum leather is lined with ridges that form hexagonal honeycomb-like patterns while rumen chamois leather is covered in small finger like projection which are flattened. The retention of the primary features of the raw materials is what gives chamois leathers their aesthetic look,[3] hence their high pricing due to high demand. Most customers are willing to pay more just to access chamois-based products since the uniqueness in the products gives them the inherent social status and ornamental value. Therefore, products manufactured from ovine stomach chamois will find a market share due to this factor.

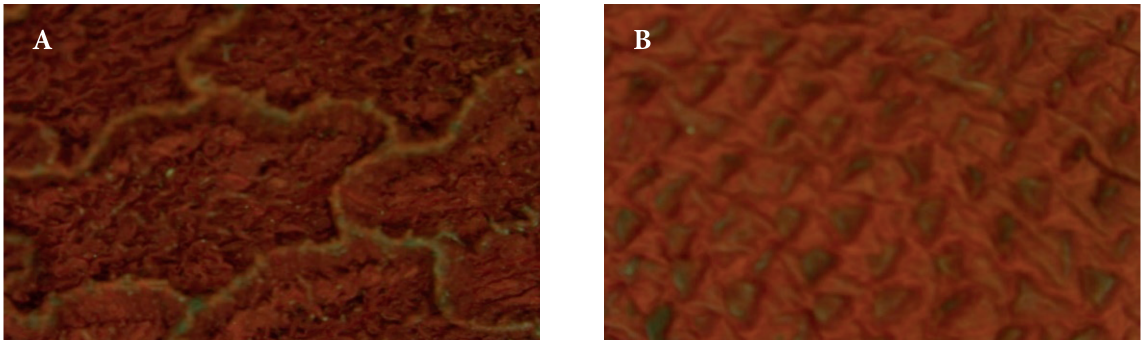

Figure 2. Optical microphotographs (16X) of stomach leather: Reticulum **(A)**, Rumen **(B)**

Figure 3. Products made from exotic ovine stomach leather: wallets and key holders

Products

The leather obtained from the ovine stomach was used for making novelty products as shown in Figure 3 below. Here, wallets and key holders were made. The results indicate that ovine stomach can be used as a source of raw material for exotic chamois leather production and subsequently for manufacturing small goods and products. In so doing, value addition to animal parts that are otherwise discarded during slaughtering[21] process will be achieved.

Conclusion

The ovine stomach, a non-conventional source of leather, was used to produce a new variety of exotic chamois grain leather. The oil tannage impacted on the softness and stretch of the obtained leathers. The thickness of the stomach increased to a reasonable degree due to shrinkage effect of the tannage. The organoleptic properties of the leathers were above average. Small products such as purses and key holders were made out of the exotic leathers. Therefore, ovine stomach can be a source of raw materials for exotic leather production.

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Research on the Production of Parchment from Turkey Skin and its Decorative Use

by
Eser Eke Bayramoğlu
Ege University, Faculty of Engineering, Department of Leather Engineering,
35100 Bornova-İZMİR – TÜRKİYE

Abstract

In this study, parchment was made of waste turkey skin and some tests were done. These tests were: Determination of thickness (TS 4117 EN ISO 2589), Determination of tensile strength and elongation (TS EN ISO 3376), Determination of tear load - Part 2: (Double edge tear) (TS 4118-2 EN ISO 3377-2), Leather - of distension and strength of grain (TS 4137 EN ISO 3379), Color fastness to water spotting (TS EN ISO 15700). Due to the low strength properties of turkey skin, a different usage area was tried to be created by making a decorative flower design. In this research, it has been tried to show how a waste material can be transformed into a product with a very high added value.

Introduction

As the world population grows rapidly, the need for animal protein is also increasing, forcing people to seek solutions to the problem. Turkey meat constitutes an alternative protein source in this context. Considering the number of turkeys in the world, it is seen that 459,369,000 pieces were produced in 2017 and this number is increasing every year.[1] America leads the world in turkey production.

When turkeys reach a certain maturity, they are cut and processed. The skins of slaughtered turkeys are separated and seen as waste. It is usually rendered as an additive or discarded. The skin that is peeled off the animal's back is seen as a very cheap item or garbage.

Turkey breeds are generally divided into five (white, yellow, bronze, black and hybrid) and the weight and some structural characteristics of the animals may vary according to their breeds. Hybrid breeds can reach around 20 kg when slaughtered. During turkey slaughter, the animal is usually skinned and separated from the carcass. Skin color in turkeys can vary from creamy white to yellowish white, depending on breed.

It has been determined that the fat content of turkey skin is 81.00% in the body part and 32.48% in the foot part.[2] It is known that the fat rate in goat skins is 3-10%, and the fat rate is up to 30% in sheep skins.[3] The fat rate Angora goat skins was determined as 11.54%.[4] In this context, it is understood that turkey skins have an extremely fatty structure, and a very good degreasing process is required.

When turkey raw skins are examined, it is striking that their structural features are similar to ostrich skins. Ostrich leather is included in exotic leathers and is used in the production of luxury consumer goods, and it is transformed into designs with very high added value.[5]

However, it was observed that the skins were cut into pieces and peeled off in turkey slaughterhouses. For this reason, the cut parts

Figure 1. Production of bags from ostrich skin with the collaboration of Eser Eke Bayramoğlu and Cem Varsoy [5]

Corresponding author email: eser.eke@ege.edu.tr or eserekebay@gmail.com
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were used in our research and the leather could not be processed as a whole.

In this study, turkey skins were processed as parchment and various properties were examined. Although parchment is a material developed for writing on leather, it has been used for decorative purposes in recent years. When parchment is used for decorative purposes in the production of yacht upholstery, various souvenirs and ornaments, its added value increases considerably.[6] For this reason, in this study, it has been shown that a raw material that is seen as waste by producing decorative linden flowers from the obtained parchment is transformed into a product with high added value.

Material and Methods

Material

Turkey skins were obtained from Pınar meat company. Turkey skins were obtained from Canadian origin white feathered turkeys weighing about 5-6 kg after slaughter. In general, it was observed that the skins were cut into pieces rather than as a whole, and there were tendons and bones in the foot parts. Pieces of skin on the body parts of turkey skins were used in the making of parchment.

Figure 2. Turkey skins preliminary trials

Figure 3. Toggling of parchment

Method

Physical tests

Some tests were applied to the parchment skins that were produced. These tests were: Determination of thickness,[7] Determination of tensile strength and elongation,[8] Determination of tear load - Part 2: (Double edge tear),[9] Leather - of distension and strength of grain, [10] Color fastness to water spotting.[11]

Figure 4. Determination of tear load

Table I

Parchment Recipe

Process	Material	%	°C	Time	pH	Notes
Wetting back	Water	200	20			
	Borron SE (TFL)	0.5				
	Borron SAF (TFL)	0.5				
				20'		Over night automation in drum
						Morning drain-wash
Liming	Water	500	25			
	Lime	6				
	Na_2OH	0.15			12.5	
	Erhavit SP (TFL)	1		15'		6 days automatic in the paddle
	Water	300				Washing
	Sellatan CF (TFL)	2		60'		
						Drain-wash
						Toggling
Flashing by hand						

Linden Flower Designs from Parchment Leather

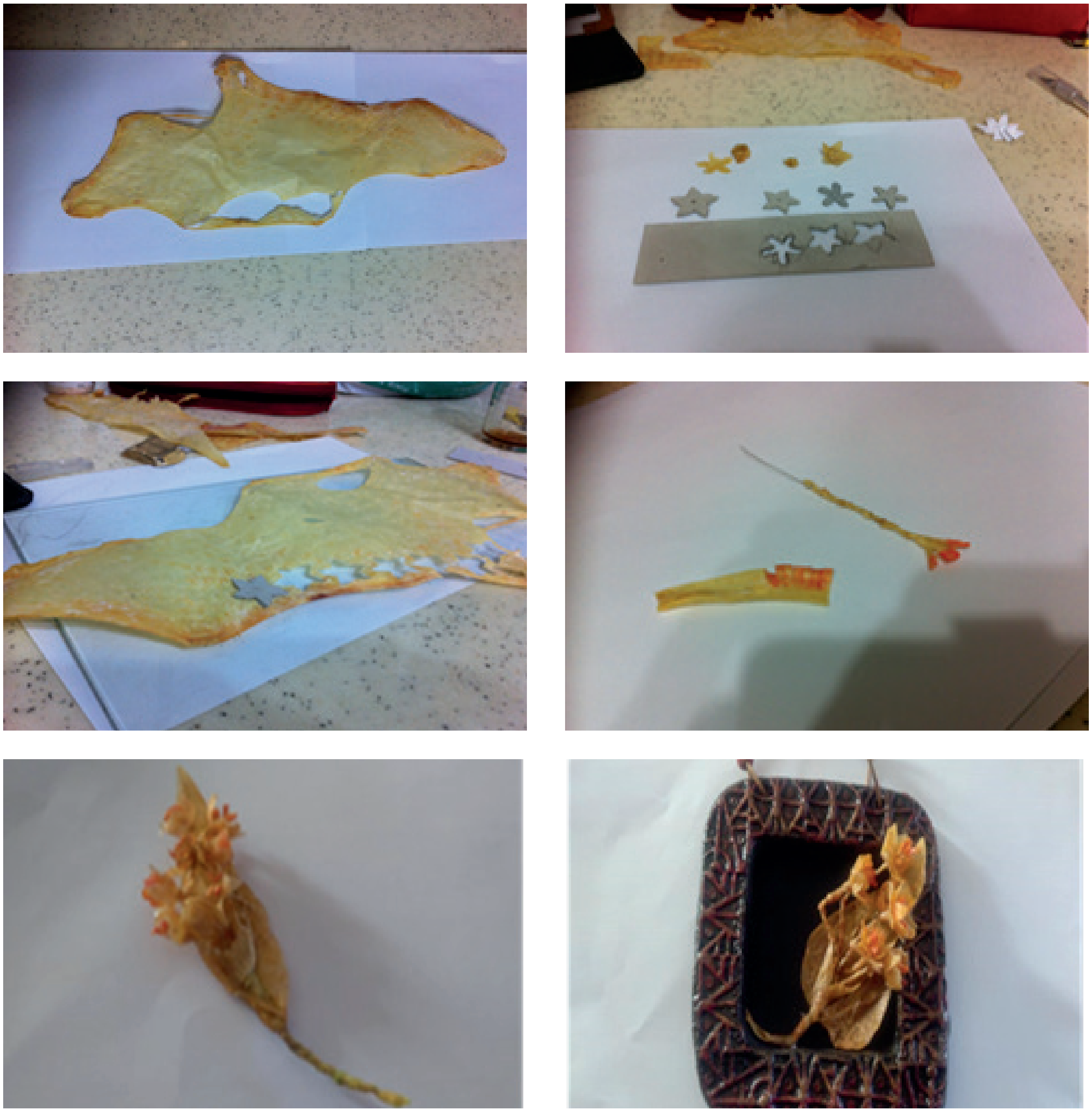

Figure 5. Making parchment linden flowers (by Nilgün Kayahan Kolan)

Results and Discussion

The amount of fat contained in the skin according to the animal species and the composition of the fat differ in different regions of the skin according to race, age, climate and nutrition. The fat content in bovine hides varies between 2-7% of the dry weight of the leather. High-energy fattening cattle hides have a high fat content, and the hide has a loose structure. The fat ratio in goat skins increases to 3-10% and up to 30% in sheep skins.[3] It has been determined that the fat content of turkey skin is 81.00% in the body part and 32.48% in the foot part.[2] As the fat content in the animal increases, the skin gains a looser structure. The high fat content in turkey skins is an indication that the skins will be loose.

The physical strength of the leather is not important in the making of some ornaments. For this reason, in this study, a decorative product was developed by making parchment from turkey skin.

In this study it was obtained that average thickness of turkey parchment was 0.42 mm, average elongation at break was 5.63%, average tensile strength was 2.44 N/mm^2, average double edge tearing was 3.30 N.

Figure 6. Use of decorative linden flower as collar decoration (by Eser Eke Bayramoglu)

Table II

Results of tensile strength and elongation

Turkey Parchment	Tensile strength (N/mm²)	Elongation (%)
Sample 1	1.59	6.61
Sample 2	3.61	5.70
Sample 3	2.35	6.31
Sample 4	3.17	5.02
Sample 5	1.46	4.49
Average	**2.44**	**5.63**

Table III

Results of Distension and Strength of Grain

Turkey Parchment	Cracking		Bursting	
	Kgf	mm	Kgf	mm
Sample 1	0	3.90	0	4.50
Sample 2	0	2.74	0	4.30
Sample 3	0	3.24	0	4.96
Sample 4	0	3.18	0	4.98
Sample 5	0	3.16	0	4.99
Average	**0**	**3.24**	**0**	**4.75**

Table IV

Results of Double Edge Tear Load

Turkey Parchment	Thickness (mm)	Tear load (N)
Sample 1	0.48	2.38
Sample 2	0.67	3.45
Sample 3	0.35	3.04
Sample 4	0.42	4.62
Sample 5	0.19	3.03
Average	**0.42**	**3.30**

Table V

Results of Color fastness to water spotting comparing with goat parchment

	Color fastness to water spotting (Grey Scale)	
	Half an hour	16 hours
Goat Parchment (Kolan,2019)	3	3
Turkey Parchment	5	5

Goat parchment thickness was 0.5 mm, tensile strength 79.9 N/mm², elongation at break 18.5%, Double edge tearing 38.7 N, cracking 37 Kgf and bursting 42.6 Kgf.[12]

It was determined that while stains were formed in the water drop test on the goat parchment, there was no stain on the turkey parchment in the water drop test (Table V).

Changes in the strength of the finished leather may vary depending on the structure of the animal, as well as the methods and chemical substances applied in leather processing. Due to the excessive fat content in the turkey skin, a parchment with low strength was obtained.

According to Unido (1994), the lowest tensile strength value recommended for chrome-tanned clothing leather is 10 N/mm². The maximum elongation value specified by Unido (1994) for chrome-tanned clothing leather is 60%. Unido (1994) for single edge tear in leathers stated at least 14.71N/mm² for chrome tanned clothing leathers.[13]

When the results obtained in the research are examined, it can be said that the strength values of turkey parchment are very low. For this reason, its use in decorative flower making was designed due to its fine structure and it was tried to obtain products with high added value.

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High Performance Leather based on in Situ Formation of Reduced Graphene Oxide in Chrome Tanning

by

Xinle Yang,[1] Yanchun Li,[1]* Mao Yang,[1] Xugang Dang,[2] and Shan Cao[1]
[1]*School of Light Industry and Engineering, Qilu University of Technology (Shandong Academy of Sciences),*
No.3501 Daxue Rd, Changqing District, 250353, Jinan, Shandong Province, China.
[2]*Institute for Biomass and Function Materials & National Demonstration Centre for Experimental Light Chemistry*
Engineering Education, School of Bioresources Chemistry and Materials Engineering,
Shaanxi University of Science and Technology, Xi'an, 710021, China.

Abstract

A novel method of high performance leather prepared via in situ reduction of graphene oxide after tanning was proposed in this research. First, nano-graphene oxide (GO) was prepared by an improved Hummers method. Then, the prepared GO was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Finally, GO was added during the chrome tanning process, and GO was reduced by ascorbic acid after the chrome tanning was completed. Moreover, the shrinkage temperature, tensile strength, tear strength and thermal conductivity of the finished leather were investigated. The results showed that the absorption of chrome tanning agent was significantly improved by the addition of GO. The tensile strength, tear strength, and the thermal conductivity of the resulted leather obviously surpassed the leather tanned by chrome tanning agent. Specifically, the tensile strength and tear strength of the leather reached 21.25 MPa and 163.95 $N\cdot mm^{-1}$, respectively, when the amount of reducing agent was ten times the amount of GO. A combination of the tanning of leather and the in situ reduction of GO is expected to become a new processing method for preparation of high performance.

Introduction

Nanomaterial refers to the material in which at least one of the two phase microstructures has a one-dimensional scale up to the nanometer scale.[1] Nano-particle phase consists of a small number of atoms or molecules. Due to the small size and large specific surface area of nanoparticles, the quantum effect and surface effect endow nanomaterial with a variety of special properties.

With the rapid development of nanotechnology, the applications of nanomaterial in leather have been further studied.[2] Montmorillonite and SiO_2 as tanning agents significantly improve the mechanical properties of leather.[3,4] Nano-ZnO is used in retanning for improving the antibacterial properties of leather.[5] Nano-TiO_2 used in leather finishing endow leather with self - cleaning.[6,7]

Graphene is an ideal two-dimensional nanomaterial with perfect crystal structure and excellent mechanical, thermal, optical, electrical properties.[8] The Young's modulus and fracture strength of graphene can reach 1000 GPa and 130 GPa.[9,10] The thermal conductivity of graphene is approximately 5300 W/m•K, which exceeds carbon materials such as diamond.[11,12] Graphene has excellent properties but lacks reactive groups that can undergo chemical reactions. And graphene oxide (GO), a derivative of graphene, significantly ameliorates this drawback.[13] The aqueous dispersion of GO has good stability, and the surface and edges of GO nanosheet layers contain reactive groups such as hydroxyl, carboxyl and carbonyl groups. It provides the conditions for the binding of GO to leather fibers. Besides, there are many spaces of different sizes between the fibers that comprise the primitive skin. It provides the conditions for the penetration of GO into the leather. In addition, GO has nano size effect and small size effect, thereby nano GO has the potential to be used in the leather production process.[14] At present, graphene has been mainly used in leather production as a finishing agent and tanning agent to improve the physical properties of leather and reduce the use of other leather chemicals.[15-18]

Compared with GO, graphene has better mechanical and thermodynamic properties. If graphene is combined with leather, it will further improve the physical and mechanical properties of leather. Due to the lack of functional groups in graphene, it cannot bind to collagen fibers. If the GO combined with the leather fiber is used as an intermediate, and then the reduced graphene oxide (RGO) is obtained by reducing the GO, thus the combination of graphene and leather is realized.[19,20] In addition, during the reduction process, the functional groups in GO cannot be completely removed and the conjugated structures cannot be completely restored. The better the reduction effect, the closer the physical properties of the obtained RGO to those of graphene. Therefore, RGO has better mechanical and thermal properties than GO.[21,22] Ascorbic acid (vitamin C) is a green reducing agent that can efficiently reduce GO. After the

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*Corresponding author email: qlulyc@126.com

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addition of ascorbic acid, the oxygenated group of GO was removed substantially, especially the content of C-O (epoxy and alkoxy groups), resulting in RGO.[21]

In this work, nano GO was added in the chrome tanning process, and ascorbic acid was used for situ reduction of GO after the tanning process. The positive effects of GO application for leather tanning were investigated by analyzing the physical properties of leather. It is expected that this work will improve the physical properties of the leather.

Experimental

Materials and chemicals

Powdered graphite with an average particle size of about 1.3 μm was used (Qingdao Huatai Lubrication seal Technology Co., LTD, China). Pickled cattle hide from Dezhou xinglong leather Products Co., LTD (Dezhou, China). Potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), ascorbic acid, formic acid all were reagent grade (Sinopharm Chemical Reagents Co., LTD, China). Concentrated sulfuric acid (H_2SO_4, 98%) was reagent grade (Laiyang Economic and Technological Development Zone Fine Chemical Plant, China). Sodium formate (CHO_2Na) and sodium bicarbonate ($NaHCO_3$) were reagent grade (Tianjin Guangfu Technology Development Co., LTD., China). Sodium chloride was industrial grade (Feicheng Shengli Salt Co., LTD., China). Chromium powder was industrial grade (Brother Enterprises Holding Co., Ltd., China).

Preparation of GO

A 500 mL three-end flask was placed in an ice bath (<5°C). 3 g graphite and 75 mL H_2SO_4 were added and stirred to mix well. $KMnO_4$ (9 g) was slowly added to the flask under 5°C over 20 min, kept below 5°C for 2 h, and then at 35°C for 1 h. The contents of the flask were then diluted with deionized water (140 mL) and heated to 95°C for 30 min, and then H_2O_2 (12 g) was added dropwise over 20 min. The obtained graphene oxide was washed with deionized water by centrifugation until the pH of the washing water was 7.0. The GO suspension was ultrasonic treated for 2h and centrifuged to obtain nano GO, which was dispersed by deionized water and controlled to 0.15% mass fraction of GO.

Tanning process

Pickled cattle hide was symmetrically sampled from both sides of the backbone and numbered according to ISO 2418:2005, and the tanning experiment with GO and chrome tanning agent was carried out. The amount of GO was 0.15% of the pickled cattle hide quality (good experimental conditions obtained in the previous test), the amount of chrome tanning agent was 6% of the pickled cattle hide quality, and the amount of reducing agent was 0%, 0.75%, 1.50%, and 2.25% of the pickled cattle hide quality respectively. The experiment was carried out in a small test drum (QY-I drum, Xuzhou Dongyuan Leather Machinery Factory, China), and the weight of the pickled cattle hide increased by 30% as the basis of measurement.

Table I

Experimental scheme for in-situ reduction of GO.

Number	Tanning agent dosage	Reducing agent dosage
1	6%Cr	–
2	6%Cr+0.15%GO	–
3	6%Cr+0.15%GO	0.75% ascorbic acid
4	6%Cr+0.15%GO	1.50% ascorbic acid
5	6%Cr+0.15%GO	2.25% ascorbic acid

The pickled cowhide was treated with saline solution containing an equal weight of water and 7% NaCl in a rotating drum, and the diluted formic acid solution adjusts the pH of the float to 2.5-3.0. The drum temperature was adjusted to 25°C and rotated for 15 minutes. The GO aqueous dispersion was added, the drum was rotated for 1.5h. Then the temperature was increased to 33°C to add chrome tanning agent and the drum was rotated for 1.5 h. Then, 1% CHO_2Na was dissolved with 20 times of water and added to the drum and rotated for 30min. The 10% $NaHCO_3$ solution was added several times with 20 minutes interval each time until the pH of the float reached 3.8-4.0, then rotated for 40min and left overnight. The next day the drum was rotated for 30 min and then taken out and rested.

Reduction of GO

Wet blue and equal weight of water were put into the drum, heated to 50°C and added different dosage of ascorbic acid, then the drum was rotated for 3 h. Then the leather was dyed and fat liquored according to the traditional technological process. A control sample of chrome tanned leather was prepared by conventional chrome tanning method.

Characterization

Fourier transform infrared spectra (FTIR) of the GO were scanned by an IRAffinity-1S FTIR spectrometer (Shimadzu, Japan) using KBr pellets over the wavenumber of 500–4000 cm^{-1}.

A SmartLab SE X-ray diffractometer (SmartLab, Japan) was used to examine the XRD diffraction of GO with a scanning angle of 5-80°.

A Zeiss G500 SEM (Zeiss, Germany) was used to observe the surface morphology of graphene oxide and leather fibers.

The elemental content and electron binding energy of GO and graphite were analyzed by an EscaLabXi+ X-ray photoelectron spectrometer (Thermo Fisher, USA).

Physicochemical properties of leather

The leather was conditioned (T=20°C, Rh=65%) for 24 h and then tested for physical and mechanical properties. Determination of shrinkage temperature (T_s), tear strength, tensile strength and elongation at break of leather in accordance with industry standards ISO 3380:2002, ISO 3377-2:2002, ISO 3376:2002.

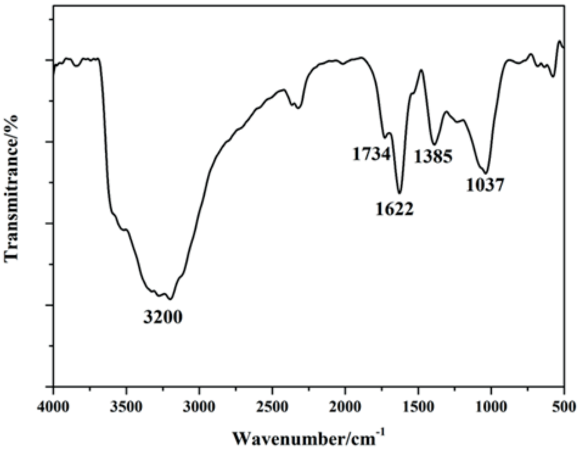

Figure 1. FTIR spectra of GO.

The Cr_2O_3 content of leather was determined using an ETHOS UP large microwave digestion instrument (Milestone, Italy) and an Avio 200 ICP-OES (PerkinElmer, USA) according to the industry standard QB/T 5315-2018.

The thermal conductivity of the leather was tested by using a Universal thermal conductivity meter TC3100 (XIATECH, China) in accordance with GB/T 10297-2015.

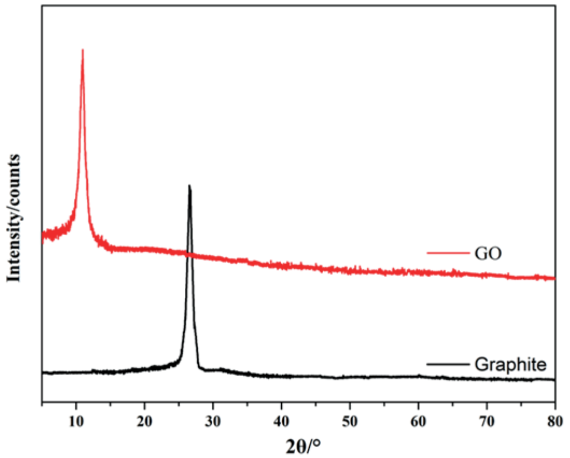

Figure 2. XRD patterns of GO and graphite.

Results and Discussion

Infrared analysis of GO

Prepared GO were analyzed by using FTIR (Figure 1). The infrared spectra showed absorption peaks of hydroxyl group (-OH) at 3200 cm^{-1}, carbonyl group (C=O) at 1734 cm^{-1}, double bond (C=C) at 1622 cm^{-1} and carboxyl group (-COOH) at 1385 cm^{-1} and epoxy bond (-C-O-C-) at 1034 cm^{-1}, indicating the successful preparation of GO containing -OH, C=O, -COOH and C-O-C groups.[23]

XRD analysis of GO

Figure 2 shows the XRD patterns of graphite and prepared GO. In Figure 2, the graphite has an obvious diffraction peak at 2θ = 26.7°. The sharp peak indicates that the graphite has high crystallinity. After oxidation, the characteristic diffraction peak of graphite disappears, and a new diffraction peak appears near 2θ = 10.8°. The layer spacing increases to 0.817 nm, which is larger than 0.335 nm of graphite. In the process of graphite oxidation, the carbon atom layer is connected to carboxyl, hydroxyl, epoxy and other oxygen-containing functional groups. The functional groups cause the carbon atom layer to fold, and water molecules are inserted between the layers, thereby increasing the distance between the carbon atom layers.[24]

Morphology analysis

The SEM of GO is shown in Figure 3 (a). GO is a sheet-layer structure full of wrinkles, indicating that GO was successfully prepared through oxidation and exfoliation processes. In Figure 3 (b), it shows that GO are uniformly distributed in the collagen fibers. Figure 3 (c) shows the thin GO sheet layers are wrapped around the collagen fiber bundle. The insertion of GO can increase the space between the fibers, which will facilitate the penetration of tanning agents and be beneficial to improve the performance of the leather.

XPS analysis of GO

The elemental composition and chemical functional groups of graphite and GO were tested using XPS, and the results are shown in Table II and Figure 4. It can be seen from Table II and Figure 4(a) that the oxygen content of GO increased significantly and the

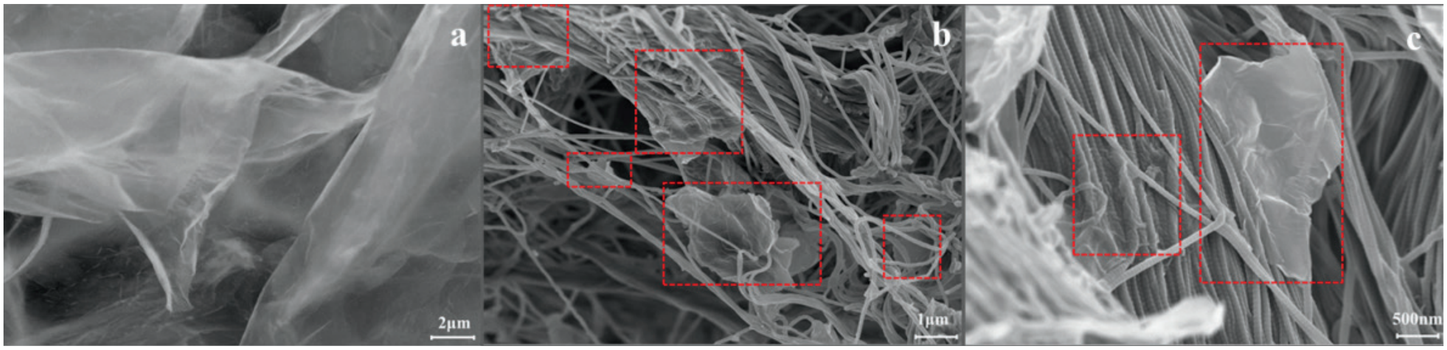

Figure 3. **(a)** SEM images of GO; **(b)** **(c)** SEM images of leather fibers.

Table II

Chemical composition of graphite and GO.

	Elemental content/%		
	C	**O**	**C/O**
Graphite	96.31	3.69	26.10
GO	70.52	29.48	2.39

ratio of C/O decreased from 26.10 to 2.39 compared to graphite. The decreased C/O ratio indicates the successful insertion of oxygen-containing functional groups into the graphite lamellar structure during the oxidation process.

Figure 4 (b) shows XPS spectra of C1s of GO. As shown in Figure 4 (b), the peaks of the four peaks are 287.4, 286.8, 285.3, and 284.6eV, corresponding to –COOH (26.62%), C=O (27.12%), C-O (27.52%), C-C/C=C (18.74%), respectively. This also indicates that after the graphite was oxidized, the carbon layer contained a large number of hydroxyl, carboxyl, carbonyl, and epoxy groups.[25]

Physical - mechanical properties testing of leather

Physical-mechanical properties of leather are shown in Table III. The application of GO can effectively improve the mechanical properties of leather. The tensile strength and tear strength of leather are increased from 14.30 MPa and 93.47 N•mm^{-1} to 17.58 MPa and 121.20 N•mm^{-1}, respectively.

After the addition of ascorbic acid, GO is reduced by removing a large number of epoxy and carboxyl groups. The large amount of RGO improves the performance of the leather. The tensile strength and tear strength of the leather are increased to 21.25 MPa and 163.95 N·mm^{-1}, respectively.

During the infiltration process, part of GO was present in the middle of collagen fibers and on the surface of bare skin in the form of physical adsorption. The GO between collagen fibers has no real binding to collagen but has a filling effect.

GO can also form chemical bonds with collagen fibers. The hydroxyl group (-OH) of GO is hydrogen bonded to the peptide bond (-CO-NH-) of collagen fibers; while the amino group (-NH_2) and carboxyl group (-COOH) of collagen fibers are hydrogen bonded to the oxygen atom of GO. The chemical combination and the nanometer effect of GO and their synergies lead to preliminary tanning of the leather, and also increases the space between the leather fibers, which facilitates the penetration of the chrome tanning agent.[26] In addition, the chrome tanning agent forms complexes with GO, which increases the molecular weight of the chrome complex and improves the absorption rate of the tanning agent.

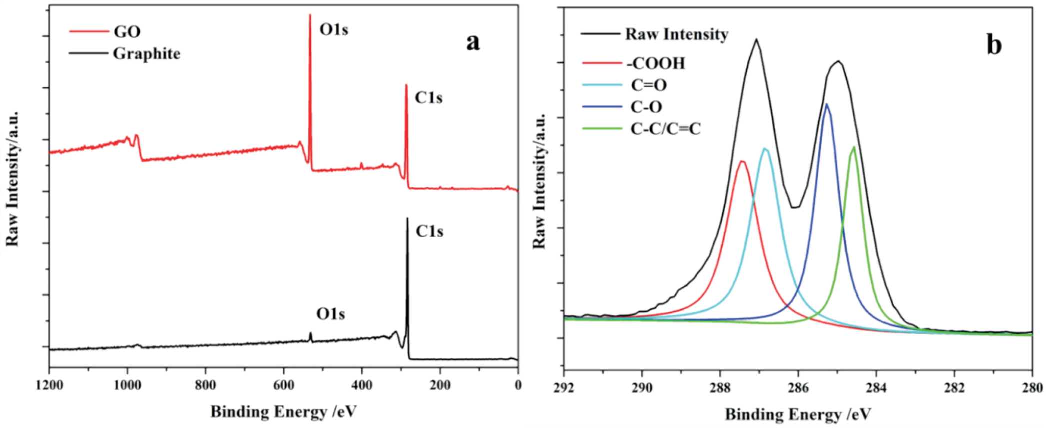

Figure 4. **(a)** XPS spectra of GO and graphite, **(b)** XPS spectra of C1s of GO.

Table III

Physical - mechanical properties of leather.

Number	**Ts/°C**	**Tensile strength/MPa**	**Tear strength/N·mm^{-1}**	**Content of Cr_2O_3/%**	**Elongation at break/%**
1	96.8	14.30	93.47	1.92	30.0
2	97.3	17.58	121.20	2.15	32.5
3	97.5	20.37	148.37	2.20	35.5
4	97.8	21.25	163.95	2.21	36.0
5	97.8	17.45	149.27	2.16	34.5

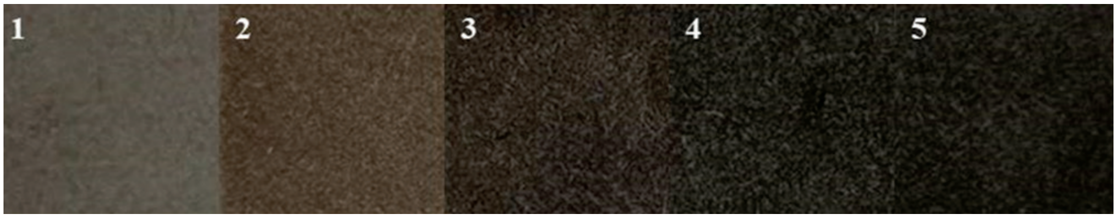

Figure 5. Pictures of leather surfaces

After adding the reducing agent, the unreacted oxygen-containing functional groups of GO are substantially removed and reduced to RGO with better physical properties. At the same time, the functional group of GO combined with collagen fiber will fix RGO and prevent it from agglomeration, so that RGO can keep uniform dispersion in the fiber, thus improving the physical and mechanical properties of leather. However, excess reducing agent will remove the oxygen-containing functional groups of GO bound to collagen fibers, resulting in RGO easily agglomerated and physical and mechanical properties reduced. In summary, the physical-mechanical properties of the leather can be effectively improved by using a reducing agent that is ten times the amount of GO.

Thermal conductivity testing of leather

As can be seen in Figure 5 and Figure 6, the color of the leather changed from blue to brown and the thermal conductivity decreased from 0.1064 W/m•K to 0.1052 W/m•K after the addition of GO. The GO combined with collagen fibers in turn reduces the thermal conductivity of the leather. Because after the graphite is oxidized, its oxygen atom content is increased as well as improving the space between the carbon atom layers, leading to the decrease of GO thermal conductivity.[27] After adding ascorbic acid, the thermal conductivity of the leather increased to 0.1127 W/m•K while the color of the leather changed from brown to black. It indicates that the ascorbic acid successfully reduced the brown GO to black RGO, the π-π conjugated structure was restored thereby improving the thermal conductivity.[20]

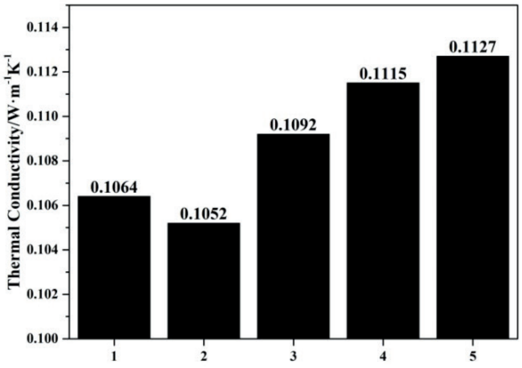

Figure 6. Thermal conductivity of leather.

Conclusions

In this work, GO was prepared by improved Hummers method and characterized by FT-IR, XRD, SEM, and XPS. It finds that hydroxyl, carboxyl and epoxy groups exist in GO. GO dispersion is used in the chrome tanning process, and ascorbic acid is used for situ reduction when the tanning is completed. GO is reduced by the addition of ascorbic acid, consequently improving the physical properties of the leather. The tensile and tear strengths of the leather increased to 21.25 MPa and 163.95 N·mm^{-1}, the thermal conductivity increased to 0.1127 W/m·K, and the tanning agent utilization increased compared to the chrome tanned leather. The results show that the reduction of graphene oxide within the leather improved the tensile and tear strengths and thermal conductivity of the leather. Therefore, this paper provides a new idea of GO application to prepare high physical properties of thermally conductive leather.

Acknowledgments

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Stahl's innovations driven by sustainability

With the rise of both electric and self-driving, cars are becoming quieter and anti-squeak and rattle materials are becoming increasingly important. At the same time, improved anti-stain performance is required, because of the current trend for pale-colored car seats. Therefore, we have developed Stay Clean. This low-VOC coating technology protects pale-colored leather and vinyl surfaces against common stains, such as dye from jeans, spilled coffee and dirt. Our solution also makes surfaces low-squeak, which is a great asset as global research has shown that a squeaking car interior is one of the biggest annoyances among car owners. Another trend in car interior is the popularity of matt surfaces. Therefore, we have developed PolyMatte®. This non-squeaking solution provides a luxurious feel to the finished article in combination with flexibility and scratch and abrasion resistance. Our portfolio contains many products, varying from beamhouse products, tanning systems to finishes, duller concentrates, crosslinkers and thickeners to leveling agents, defoamers, colorants and hand modifiers. Our most sustainable option is Green PolyMatte®, which is based on rapeseed oil (20%) instead of crude oil-derived intermediates. If you would like to know what our Stahl solutions for automotive can do for your business, please visit **www.stahl.com** or contact us at: **alexander.campbell@us.stahl.com**.

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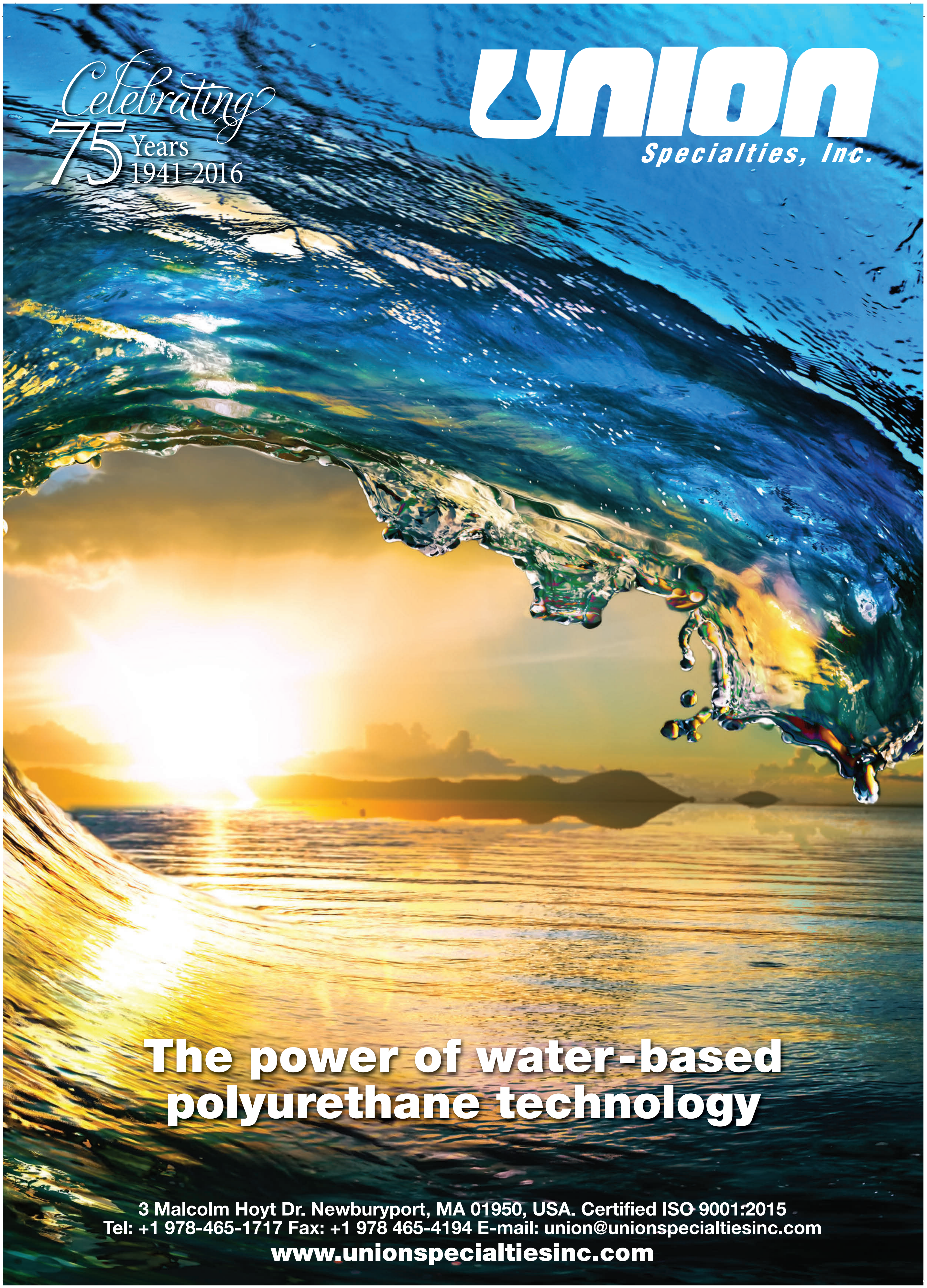


COUNCIL CONFERENCE CALL MINUTES
AMERICAN LEATHER CHEMISTS ASSOCIATION SPRING COUNCIL MEETING
March 10, 2022

PRESENT

Officers:	Mike Bley, Joe Hoefler
Council Members:	Jose Gallegos, Steve Lange, John Rodden
Executive Secretary:	Carol Adcock
Convention Chair:	Bill Clippinger

1. **WELCOME**. President Mike Bley called the meeting to order. A quorum was present.

2. **CONVENTION STATUS UPDATE.**

Convention 2022

Bill Clippinger, Convention Chair for 2022, reported that overall schedule as given out for the November 11, 2021 Council Meeting had not changed. As stated in the November meeting, bowling at Kegler's is scheduled for Wednesday evening, June 22. There will be an open bar and food plus darts, pool tables and bowling.

Financial Campaign

Donis Bosworth, Convention Vice Chair, is in charge of the financial campaign. It will be the same as the 2019 convention. She emailed everyone to say she was having trouble with commitments since there was no 2020 convention and some had already committed to sponsor and paid. Council felt that hopefully past sponsors would realize that under the present circumstances with covid keeping the ALCA from having a convention for 2020 and 2021, there was a real need to support the 2022 convention and move forward. After the meeting, Council was emailed the 2022 financial sponsorship campaign that outlines the various sponsorships and benefits given.

Discussion was held concerning given discounts for the convention. Motion was made, seconded and unanimously approved to give a discount of $50 for companies sending two or more individuals who are paying the regular convention registration fee.

Technical Program

Joe Hoefler reported that he has 5 fairly firm presentations. There are still some people unsure about traveling overseas. Other possible presenters were recommended. Council is to help Joe obtain more papers.

Alsop Award

The recipient of the Alsop Award has already been selected by the committee, chaired by Joe Hoelfer, and approved by Council.

O'Flaherty Award

The recipient of the O'Flaherty Award has already been selected by the committee, chaired by Sarah Drayna, and approved by Council.

AV Person

Mr. Clippinger will start looking for someone who can do the AV for the convention during the technical program.

Wilson Lecture – David Peters, Chair

Randy Johnson with GST AutoLeather, Inc. will present the 2022 Wilson Lecture. He was informed of the date change and has agreed to giving it on June 22. Mrs. Adcock contacted him about a name change for his company and made that change in the advertisement on the inside back page of the *Journal*. Since Mr. Peters has retired, Mrs. Adcock will be handling the Wilson speaker, but things are on track for now.

2023 Convention Site

Mr. Hoefler read a letter he received from Stephen Sothmann. Mr. Sothmann has asked Council to not select a 2023 convention site until he can talk to them during the 2022 convention. Council agreed to wait on picking a site for the 2023 convention.

3. **FINANCIAL REPORT –** Carol Adcock

Council was sent the 2021 Profit & Loss Statement along with the Balance Sheet for the year. There was no Budget vs. Actual Report as Council never set a budget for 2021. The P&L showed a profit of $24,546.75. The 2021 financial analysis has not been done yet.

Motion was made, seconded and carried to accept the 2021 financial reports.

Executive Secretary Carol Adcock reviewed the 2022 Membership, Dues, Subscriptions and Journal Advertising report as of March 7. There are a total of 266 members at the present time including SLTC members participating in the Journal exchange. She mentioned that the annual analysis of the books had not been done. After the meeting, the financial analysis was completed and sent to Council for approval. It is attached to these minutes.

A list of unpaid dues was also reviewed. All will be dropped from the Association per the by-laws as of April 1. The income from dues and subscriptions was reviewed.

Mrs. Adcock reported that 5 advertisers committed for 2022 journal advertising, with all being paid.

4. **TECHNICAL COMMITTEE REPORTS**

There were no technical committee reports at this time.

5. **EDITOR'S REPORT –** Steve Lange

Mr. Lange reported that he has papers through the September 2022 issue so this is doing really well. He would like more reviewers and asked Council for any suggestions. He has had three more years of *Journal* scanned to put on the journal website.

Motion was made, seconded and unanimously passed to accept the Editor's Report.

6. **OTHER COMMITTEE REPORTS**

2022 Slate of Candidates

The Nominating Committee has a firm candidate for Vice President. Since the chair of the committee has retired, a new chair for the committee was needed. Motion was made, seconded and unanimously passed to appoint John Rodden as Chair of the 2022 Nominating Committee. They hope to have the four Council candidates by the end of March or early April. The two councilor candidates that did not win in the last election will be contacted to see if they would run again.

Ways & Means Committee – Shawn Brown and Steve Schroeder
Mr. Brown submitted awritten report prior to the meeting. It was as follows:

March 9, 2022
Here is some of the highlights and overall review of the plan:
Balance on January 1, 2021: $ 198,658.70
Withdrawals during 2021: $47,978
Ending balance on December 31, 2021: $ 198,875.08
The portfolio had growth of approximately $ 48,000 for year 2021 - which would equate to an approximate return of + 24.13 % for year 2021.

Current balance as of March 8, 2022 is: $ 173,234.26 (down about 12 % for year 2022 - as a comparison, the NASDAQ Index is down nearly 16 % and the S&P 500 Index is down approx. 11 % year to date in 2022)

Current allocation is:
Approx. 18.5 % - Home Depot stock - and this is a large part of the portfolio being down in 2022 as Home Depot stock is down – 21.67 % year to date in 2022

Mutual funds allocation:
Approx. 18 % is in Growth Fund of America (growth / equity oriented)
Approx. 30 % is in American Balanced Fund (which is 50 % growth / equity and 50 % cash / money market / fixed income bonds)
Approx. 26 % is in Washington Mutual Fund (which Is a value oriented, blue chip, high dividend paying fund with a growth / equity / value-oriented blend)
Approx. 7.5 % is in money market / cash account

Overall profit on the account - despite all the withdrawals and the crazy market volatility is: total invested: $ 107,158.57 - and current value is $ 173,234.26 (still way ahead of the game in spite of this Covid, Ukraine, Putin craziness)

The portfolio managers are not suggesting any changes to the allocation of the portfolio at this time, they feel the portfolio is well positioned.
Best Regards,
Shawn Brown

Motion was made, seconded and unanimously passed to accept the Ways and Means Report as written.

7. **OLD BUSINESS**
No old business came before the Council.

8. **NEW BUSINESS**
No new business came before the Council.

Location and Date of Next Council Meeting
The next council meeting will be the regular meetings held during the convention. The current council will meet on Tuesday, June 21, at 9:00 a.m. in the Hickory Board Room. The old and new Council will meeting on Thursday, June 23, at 8:00 a.m. in the same room.

There being no further business before Council, the meeting was adjourned.

Respectfully submitted,
Carol Adcock, Executive Secretary

SCOTT NORTHAM, CPA, PC
Certified Public Accountants

INDEPENDENT ACCOUNTANT'S REPORT ON APPLYING AGREED-UPON PROCEDURES

American Leather Chemists Association
1314 50th Street, Suite 103
Lubbock, TX 79412

We have performed the procedures enumerated below, which were agreed to by American Leather Chemists Association (ALCA), solely to assist you in evaluating the revenue and expense transactions of the Organization for the fiscal year ended December 31, 2021. ALCA's management is responsible for the presentation of the revenue and expense transactions. This agreed-upon procedures engagement was conducted in accordance with standards established by the American Institute of Certified Public Accountants. The sufficiency of these procedures is solely the responsibility of those parties specified in this report. Consequently, we make no representation regarding the sufficiency of the procedures described below either for the purpose for which this report has been requested or for any other purpose.

We examined the detailed general ledger and a representative sample of the revenue and expense transactions and the related underlying supporting documentation for the organization for the fiscal year ended December 31, 2021 for the purpose of determining whether the documentation presented properly supported the revenue and expense transactions and were properly categorized within the financial records. We found no significant exceptions within the revenue and expense transactions tested.

We were not engaged to conduct, and did not conduct, an examination, the objective of which would be the expression of an opinion on the financial statements of the Organization. Accordingly, we do not express such an opinion. Had we performed additional procedures, other matters might have come to my attention that would have been reported to you.

This report is intended solely for the information and use of by the directors and management of American Leather Chemists Association and is not intended to be and should not be used by anyone other than those specified parties.

SCOTT NORTHAM, CPA, PC
Ruidoso, New Mexico
March 24, 2021

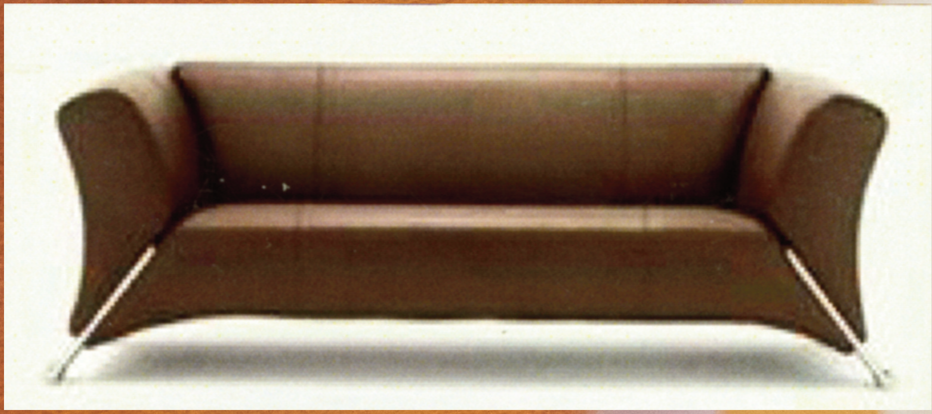
1035 Mechem Drive
Ruidoso, NM 88345

(575) 258-5559
FAX (575) 258-5570

LEATHER

AVELLISYNCO

Selected Dyestuffs



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Lifelines

Sultan Çivi, graduated from Ege University, Faculty of Engineering, Department of Leather Engineering. Worked in the finishing department of Kazım Süren Leather Tannery and Karakoç Chemical companies. Currently a PhD student in the same department. Area of expertise is leather finishing and finishing chemicals.

Eser Eke Bayramoğlu, see *JALCA* 115(1), 30, 2020

Liang Jia, has a Master's degree and works at the Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, P. R. China. E-mail:1114151647@qq.com

Jing Li, has a Doctorate degree and works at the Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, P. R. China. E-mail: lijingzhengzhou91@163.com

Li Wang, has a Doctorate degree and works at the Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, P. R. China. E-mail:wangli9403@163.com

Jun Xiang, is a Professor at the Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, P. R. China. E-mail: junxiang@scu.edu.cn

Yi Chen, is a Professor at the Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, P. R. China. E-mail: chenyiscu@163.com

Haojun Fan, is a Professor at the Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, P. R. China. E-mail: fanhaojun@scu.edu.cn

Peris N. Wainaina, is an accomplished leather technologist with a strong professional background in Leather Technology with over five years of experience in technical, research and training, currently working as Principal Leather Industrial Development Officer at Kenya Leather Development Council. She holds a Master of Science Degree from Dedan Kimathi University, having completed her studies in leather technology in 2019. Her research area is in leather technology with specialty in leather processing, value addition, manufacturing and environment. She has skills in leather processing, leather products development and physical and chemical tests of leather. One of her outstanding research projects that made significant contribution in the leather field is on oil tannage using oil extracted from tannery fleshing waste. She has two publications in peer reviewed journals on leather technology and environment. She is committed in her career development in order to ensure quality research and innovation in the long-term.

Benson Ongarora, is an accomplished chemistry lecturer with over seven years of experience in teaching and research in the Department of Chemistry at Dedan Kimathi University of Technology. He holds a doctorate degree from Louisiana State University, having completed his studies in organic chemistry in 2012. His specialty in organic chemistry has provided him with a good foundation in material chemistry. He has skills in synthesis, isolation, characterization and analysis, which have catapulted him to carryout research in various fields. He has successfully supervised four students at Master's level both in the area of chemistry and leather technology. One of his outstanding research projects in leather technology is on tannage of chamois using oil extracted from tannery fleshing waste. He has more than ten publications in peer reviewed journals on various subjects. He is committed in his career development in order to ensure quality research and innovation in the long-term. He is a reviewer with Team Publons, a part of Web of Science group, besides reviewing for the Journal of the American Leather Chemists Association (*JALCA*). He believes that technology will go a long way in solving challenges faced by the society

Paul Tanui, is a lecturer with over nine years of experience in teaching and research. He started his teaching and research career in the Department of Chemistry at State University of New York at Binghamton, NY. Here in Kenya, he has been teaching and researching in the Department of Chemistry at Dedan Kimathi University of Technology since 2017. He holds a doctorate degree from SUNY Binghamton, having completed his studies in organic chemistry in 2012. His research area is in organic chemistry with specialty in organic synthesis of biologically-relevant molecules for potential therapeutic purposes. He has skills in multi-step synthesis, purification, characterization and analysis of the target molecules. He has successfully supervised one student at Master's in the area of leather technology. He has three publications in peer reviewed journals on chemistry and leather technology fields. He co-authored a publication that made significant contribution in the leather field on tannage of chamois using oil extracted from tannery fleshing waste. The major hands-on experiences acquired are proper organic synthesis techniques in the hood including column chromatography, optimization and scale-up multiple-steps of synthetic routes, adequate understanding and use of UV-Vis Spectrometer, RNA/DNA Synthesizer, and HPLC. His extensive research and teaching skills comes a long way in building a better workforce through training and capacity building.

Xinle Yang, a postgraduate student in the School of Light Industry Science and Engineering at Qilu University of Technology, is studying clean leather production technology.

Yanchun Li, a professor in the School of Light Industry Science and Engineering at Qilu University of Technology, is studying clean leather production technology.

Mao Yang, a lecturer in the School of Light Industry Science and Engineering at Qilu University of Technology, is studying clean leather production technology.

Xugang Dang, an associate professor in the School of Bioresources Chemistry and Materials Engineering at Shaanxi University of Science and Technology, is studying the development and utilization of environmentally friendly leather chemicals.

Shan Cao, an associate professor in the School of Light Industry Science and Engineering at Qilu University of Technology, is studying clean leather production technology and waste treatment.

INDEX TO ADVERTISERS

116th ALCA
ANNUAL CONVENTION
June 21-24, 2022
Eaglewood Resort & Spa
Itasca, IL

Featuring the 61st John Arthur Wilson Memorial Lecture

"The Road Ahead"

By Randy Johnson, President and CEO

PANGEA

Formerly GST Seton

Tentative Schedule

Tuesday, June 21

Golf Tournament, Opening Reception and Dinner

Wednesday, June 22

John Arthur Wilson Memorial Lecture
All Day Technical Sessions, Fun Run
Reception and Dinner, Activities - Bowling, Pool, Darts and an Open Bar

Thursday, June 23

All Day Technical Sessions, Annual Business Meeting
Activities Awards Luncheon
Social Hour, ALCA Awards Banquet

Visit us at www.leatherchemists.org for full details under Annual Convention as they become available