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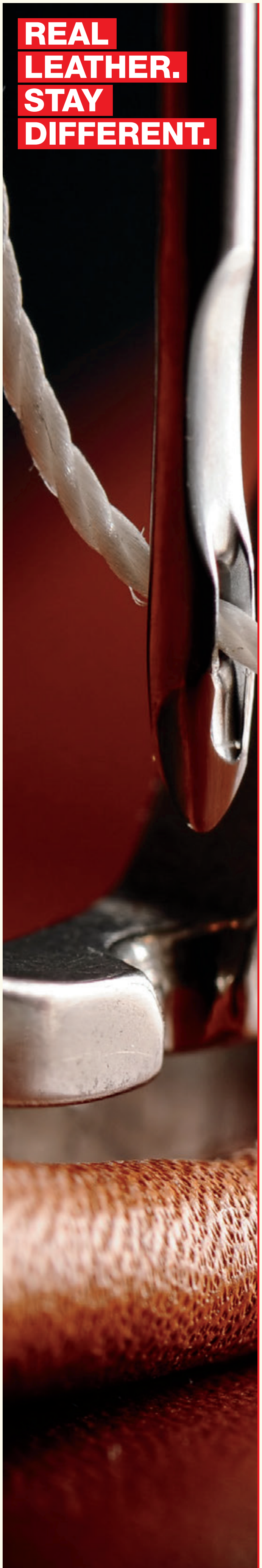

LEATHER BY NUMBERS:

FACTS AND FIGURES FROM THE US LEATHER INDUSTRY AND BEYOND

Note: All figures as of January 2021 or latest available.

ZERO cattle are killed to make US leather. US hides have been valued at JUST 1-2% of a cow's total value for the last two years, which is why they are considered a by-product and often end up as waste. The average price per head of US cattle is $2,000-2.200, while hides vary in price from $5 TO $35 PER PIECE, if sold at all. (1)

330M hides come from the meat and dairy industries around the world. Approximately **34M** were processed the US. (2) **AS MANY AS 2.4M US HIDES** ended up as landfill in 2019, this is **7%** of the national total.

Worldwide the waste figure is approximately **40%** or **132M** hides. With the average hide weighing 25Kg this means that **3M TONNES** are thrown away ever year.

Leather production turns more than **4.5M TONNES OF** potential waste, every year, into usable, durable goods. This saves **2.7M TONS OF GREENHOUSE GAS EMISSIONS** from landfill sites. (3)

Production, processing and distribution of hides and leather products directly employs an estimated **5,486** individuals, who collectively earn more than **$384M**. US exports of hides and leather was over **$1.5BILLION** in 2021. (4)

The US exports approximately **95%** of all cattle hide and wet blue leather products it produces, worth **$2.85BILLION**. (5)

Around **45%** of global leather production is used to make footwear, **22%** for clothing, bags and accessories, **18%** for car upholstery, and about **15%** for furniture. (6)

Water consumption for the production of leather from cattle hides has fallen by more than **35%** in the past 25 years, down from **60 CUBIC-METERS** per ton of hides to **38 CUBIC-METERS** per ton. US tanneries are required, by law, to connect to effluent treatment plants to prevent pollution. (7)

Leather will biodegrade in **LESS THAN 50 YEARS**. In contrast, it can take **500 YEARS** or more for synthetics, made from petrochemicals, to degrade. (8)

ReFed's conversion rate for food waste is for **EACH METRIC TON OF WASTE DISPOSAL** there is **9.8 7MT** of **CO2 EQUIVALENT** emitted. In this case, mostly as methane. (9)

This factsheet is produced by the Leather and Hide Council of America (L&HCA), established to promote the US leather industry which is responsible for a significant proportion of the international trade in hides. The L&HCA works to establish best practice in US leather production and to share this worldwide. Figures quoted refer to the USA unless otherwise stated.

SOURCE:

(1) https://downloads.usda.library.cornell.edu/usda-esmis/files/rx913p88g/w0893q25p/5d86qb66f/lstk0223.pdf

(2) https://downloads.usda.library.cornell.edu/usda-esmis/files/r207tp32d/pg15cj85z/hd76t466z/lsan0422.pdf

(3) 2020 LHCA Infographic

(4) John Dunham & Associates, Economic Impact of the Meat Industry (2016)

(5) https://thesustainabilityalliance.us/wp-content/uploads/2020/04/US-Hide-Skin-and-Leather-Factsheet-0420.pdf

(6) TBC

(7) 2020 LHCA factsheet

(8) https://en.wikipedia.org/wiki/Leather#:~:text=Leather%20biodegrades%20slowly%E2%80%94taking%2025,or%20more%20years%20to%20decompose

(9) https://insights-engine.refed.org/impact-calculator?inputs=%7B%22sector%22%3A%22manufacturing%22%2C%22type%22%3A%22fresh-meat-seafood%22%2C%22unit%22%3A%22tons%22%2C%22alternative%22%3Afalse%2C%22destinations%22%3A%5B%7B%22key%22%3A%22refuse-discards%22%2C%22current%22%3A1%7D%5D%7D

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Application of Some Plant Extracts as Biocolorants for Leather During Finishing Process

by

Roza Mirzamuratova,[1] Eser Eke Bayramoğlu[2*] and Rashid Kaldybayev[1]

[1]*M. Auezov South Kazakhstan University, Higher School of Textile and Food Engineering, Department of Technology and Design of Light Industry Products*, Shymkent, Kazakhstan

[2]*Ege University, Faculty of Engineering, Department of Leather Engineering,*
35100, Bornova-Izmir, Türkiye

Abstract

In this research, chrome-tanned bovine crust leathers were dyed during the finishing process using plant extracts: walnut shell (*Juglans regia*), oak bark (*Quercus cortex*), and onion peel (*Allium cepa*). In this study, the standard recipe applied by the factory was used in the leather finishing process. For this recipe, various plant extracts were used instead of pigments, and groups that did not contain pigment and any dyestuff were formed as the control groups.

After these processes, color measurement analyzes were performed on Konica Minolta CM 3600d spectrophotometer. In order to investigate the effects of walnut shell (*Juglans regia*), oak bark (*Quercus cortex*), and onion peel (*Allium cepa*) on the other performance properties of leather, dry and wet rub fastness test according to standard method TS EN ISO 11640 (2001) was performed. The results of the study were statistically evaluated using the NCSS method (Number Cruncher Statistical System). As a result of the study, it was noticed that, depending on the extract, different colors were obtained. It was found that the dry and wet fastness of leathers treated with plant extracts improved.

Introduction

The concept of sustainability has gained importance in leather industry applications as well as in all industrial production.[1] Formally referred to as sustainable production and consumption; the notion concerns with the production and consumption of products, services, and resources in a manner that is environmentally benign, economically viable, and socially beneficial. Within the scope of sustainable production, the use of herbal products in various stages of leather processing have gained importance.[2-10] In addition, research on the use of waste herbal products has intensified and it has been scientifically proven to have many advantages such as elimination of free formaldehyde or reduction of hexavalent chromium formation etc.[11-14] In this way, the use of waste plant products is very important for sustainable production, both to prevent environmental pollution and to create economic value.

The finishing process can give the leathers many different properties, as well as the coloring process for dyed or undyed leathers. The desired surface properties (color, dull or glossy appearance, burning effects, 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.) become available for sale.[15] The oak tree has a special importance from the point of view of tanners, compared to other trees, the history of which has been going on for many years.[16] To protect the environment, it is necessary to investigate a more environmentally friendly leather treatment.[17]

In this study, onion peel, oak bark and walnut shell were taken and extracted, and the prepared extract was used instead of pigment in the finishing process. In this way, its usability as a dyestuff was investigated. As far as our research on literature, this work has not yet been studied and has no analogues, so research in this area is important.

Experiments

Materials and Methods

For the study, undyed chrome-tanned bovine leathers processed by the Turan-Skin factory, located in Kazakhstan in the city of Shymkent, were used.

The plants picked from various regions of Kazakhstan were first dried and then ground.

100 grams of dried plant material were mixed with 3000 grams of distilled water and boiled for 3 hours over low heat. The resulting liquid was cooled and filtered. The amount of pH in a liquid dye solution is shown in Table I.

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

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Table I

pH value of extracts and chemical pigment

№	Dye Solution	pH
1	Walnut shell (*Juglans regia*)	5
2	Oak bark (*Quercus cortex*)	3.5
3	Onion peel (*Allium cepa)*	4.5
4	Chemical pigment	6.5

Plant extracts were used during the finishing. During the finishing the look and function of the leather was defined, its surface was protected. This made it a delicate and important phase, where we decided to invest in order to develop an increasingly eco-sustainable production. During the finishing, binders, waxes, pigments and dyestuffs were applied to the grain of the leather in order to impart the color, give a good surface and other organoleptic, physical and commercial characteristics. The finishing was carried out by spraying, the process consisted of two stages. The first stage was coating dyeing, the second stage was fixing the coating with lacs and dyestuffs. The finishing process was carried out using different dyestuff options:1) natural extracts (walnut shell, oak bark, onion peel); 2) chemical pigments. The finishing recipe is shown in Table II.

The experiment was carried out three times.

As a result, 5 types of samples were used for the study, of which 3 were made with plant extracts (walnut shell, oak bark, onion peel) and 2 control samples were made with chemical pigment and water.

All leathers were conditioned for reproducible testing in the laboratory under the same conditions (20±2°C, 65±2% RH).

Color Measurement Tests of Leather Samples

Determination of color fastness was carried out on a Konica Minolta CM 3600d spectrophotometer. The measurements were carried out by reading 5 points (4 corners and 1 middle) from the surface of the

Table II

Finishing recipe used in application

Chemicals	Application Coat (gramme)	Explanations
Stage 1		
CPT 2350	150	Acrylic Binder(Alpa Chemistry)
CPT 2345	150	Binder (Alpa Chemistry)Acrylic Polymer
CPU 1641	150	Polyurethane Binder (Stahl)
CRE 1036	200	Acrylic Binder(Alpa Chemistry)
CST 6760	200	StukoWax(Alpa Chemistry)
CW 171	50	Synthetic Wax(Alpa Chemistry)
CW 159	50	StukoWax (Stahl)
CST HD	50	Polyurethane Binder (Stahl)
Dyestuff	2000	Plant Extracts (walnut shell, oak bark, onion peel) or chemical pigment or water
1) 3× spray – RotoPress (80°C, 150 Bar) – 3× spray – RotoPress(80°C, 70 Bar) – 3× spray (RotoPress 80°C, 70 Bar)		
Stage 2		
CK 1622	150	Polyurethane lacs (Stahl)
Dyestuff	300	Plant Extracts (walnut shell, oak bark, onion peel) or chemical pigment or water
1) 2× spray – RotoPress (90°C – 70 Bar)		

Table III
Color Measurement Test Results

	Data Name	L*(D65)	a*(D65)	b*(D65)	DL*(D65)	Da*(D65)	Db*(D65)	DE*ab(D65)
Control group								
1	water 1	81.46	-0.05	4.4	52.59	0.05	5.01	52.83
	water 2	79.75	0.04	4.64	50.88	0.14	5.26	51.15
	water 3	80.07	-0.41	4.32	51.19	-0.31	4.93	51.43
2	chemical pigment 1	78.61	-0.07	12.64	49.74	0.04	13.25	51.47
	chemical pigment 2	79.29	-0.16	12.68	50.41	-0.06	13.29	52.14
	chemical pigment 3	78.83	-0.09	12.8	49.95	0.01	13.41	51.72
Experimental group								
1	oak bark 1	70.55	5.79	23.9	41.67	5.9	24.51	48.71
	oak bark 2	69.09	6.28	24.36	40.21	6.38	24.97	47.76
	oak bark 3	69.99	5.99	24.1	41.11	6.1	24.71	48.36
2	onion peel 1	74.54	3.55	36.7	45.67	3.65	37.31	59.08
	onion peel 2	74.34	4.05	37.72	45.46	4.16	38.33	59.61
	onion peel 3	74.78	3.89	37.71	45.9	3.99	38.33	59.93
3	walnut shell 1	74.86	1.5	15.81	45.98	1.6	16.42	48.86
	walnut shell 2	74.64	1.61	15.65	45.76	1.72	16.27	48.6
	walnut shell 3	74.44	1.83	16.46	45.56	1.93	17.08	48.7

samples in the reading zone of the device. The results were evaluated by averaging these 5 measurement points.

Cut samples of 15 × 15 cm were used for the aging test. Color measurements were made in Minolta before the samples were aged. Before starting the measurement on the machine, black or white standards were read as a reference. Since the leather samples used for this experiment were close to white in color, the measurement was made based on the white standard.

Over time, discoloration and aging occurs on the surface of the leather under the influence of environmental factors. The purpose of the various aging methods described in this international standard is to obtain results indicating changes that may occur when exposed to the leather in a certain environment over a long period of time. According to ISO 17228-7B (2005) standard, leather samples were subjected to aging processes under 60°C and 90% humidity conditions for 24 and 96 hours in a UV cabinet whose temperature and humidity can be adjusted. Color measurement test results are shown in Table III.

The results in Table III show that the magnitude of a*(D65), Da*(D65) increased compared to the control group of the experimental group, approaching red. The indicator b*(D65), Db*(D65) moved in the direction of more yellow than the control group. Around L*(D65), DL*(D65), there is only a small difference between the control group and the experimental group.

Color Measurement Test Results after the aging process under 60°C and 90% humidity conditions for 24 hours in a UV cabinet are shown in Table IV.

Table IV

Color Measurement Test Results after aging process (24 hours)

	Data Name	L*(D65)	a*(D65)	b*(D65)	DL*(D65)	Da*(D65)	Db*(D65)	DE*ab(D65)
Control group								
1	water 1	80.35	-0.09	4.52	51.47	0.02	5.14	51.73
	water 2	78.8	0.59	4.3	49.93	0.69	4.92	50.17
	water 3	78.19	0.8	4.74	49.31	0.91	5.35	49.61
2	chemical pigment 1	78.44	-0.03	12.62	49.56	0.08	13.24	51.3
	chemical pigment 2	78.67	-0.01	12.63	49.8	0.09	13.24	51.53
	chemical pigment 3	78.52	-0.09	12.66	49.64	0.02	13.27	51.38
Experimental group								
1	oak bark 1	69.68	6.08	23.87	40.81	6.18	24.48	47.99
	oak bark 2	69.81	5.49	24.13	40.94	5.59	24.74	48.16
	oak bark 3	70.2	5.74	24.16	41.32	5.84	24.78	48.53
2	onion peel 1	74.11	4.85	37.93	45.23	4.95	38.54	59.63
	onion peel 2	73.71	4.46	37.48	44.83	4.57	38.09	59.01
	onion peel 3	75.16	4.02	36.75	46.28	4.12	37.36	59.63
3	walnut shell 1	72.77	2.09	17.31	43.9	2.19	17.92	47.46
	walnut shell 2	73.14	1.83	16.28	44.26	1.94	16.89	47.42
	walnut shell 3	74.07	1.53	15.69	45.19	1.63	16.31	48.07

Table V

Color Measurement Test Results after ageing process (96 hours)

	Data Name	L*(D65)	a*(D65)	b*(D65)	DL*(D65)	Da*(D65)	Db*(D65)	DE*ab(D65)
Control group								
1	water 1	76.84	1.50	5.12	47.96	1.61	5.73	48.33
	water 2	76.83	1.51	5.12	47.95	1.61	5.74	48.32
	water 3	76.74	0.31	7.06	47.87	0.42	7.67	48.48
2	chemical pigment 1	78.46	-0.14	12.66	49.58	-0.04	13.27	51.33
	chemical pigment 2	79.31	-0.08	13.03	50.43	0.03	13.64	52.24
	chemical pigment 3	78.64	-0.05	12.71	49.76	0.05	13.32	51.51
Experimental group								
1	oak bark 1	70.53	6.00	24.77	41.66	6.10	25.39	49.16
	oak bark 2	69.11	6.28	24.38	39.24	6.39	24.99	46.96
	oak bark 3	70.03	5.76	24.29	41.15	5.86	24.90	48.45
2	onion peel 1	75.66	3.40	35.12	46.78	3.50	35.73	58.97
	onion peel 2	75.50	3.31	35.31	46.62	3.42	35.92	58.95
	onion peel 3	76.33	3.11	36.25	47.45	3.22	36.87	60.18
3	walnut shell 1	73.91	1.75	16.62	45.04	1.86	17.23	48.26
	walnut shell 2	74.14	1.93	16.49	45.26	2.03	17.10	48.43
	walnut shell 3	73.54	1.97	17.41	44.67	2.08	18.03	48.21

There was no significant difference between the before aging process of leather and after the aging process of leather under 60°C and 90% humidity conditions for 24 hours in color.

Color Measurement Test Results after the aging process under 60°C and 90% humidity conditions for 96 hours in a UV cabinet are shown in Table V.

No significant difference was found between the before aging process of leather and after the aging process of leather under 60°C and 90% humidity conditions for 96 hours in color.

Dry and Wet Rubbing Fastness Analyses

The leather samples were made from black and white felts and tested for dry and wet fastness test according to TS EN ISO 11640 (2001) from the surface of the sample. An Otto Specth Bally Finish Tester was used for analysis. The change in color of the leather and felt samples was evaluated in accordance with A02 (1996) and ISO 105 A03 (1996) and ISO 105 with a gray scale.

Statistical Evaluation of Results

When evaluating the results of the study, statistical analysis was used NCSS (Number Cruncher Statistical System) 2022 Statistical Software (NCSS LLC, Kaysville, Utah, USA). descriptive statistics (mean, standard deviation, median, frequency and ratio).

Normal distribution of parameters between groups One-way Anova test and Bonferroni test to detect group differences; Student's t-test was used in their evaluation according to the two groups.

Between groups of abnormal distribution of parameters Wallis test and Dunn's test in identifying differences between groups; the Mann Whitney U test was used in the evaluation according to the two groups.

When comparing qualitative data, the Fisher Freeman Halton test was used. 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 application. Figure 1 shows the difference in leather samples after finishing process.

Dry and Wet Rubbing Fastness Results

In accordance with the standard method, the analysis of rub fastness of the leather to dry friction was carried out using black felt, for wet friction of the leather white felt was used. The results were evaluated on a gray scale. Dry rub fastness test results are shown in Table VI.

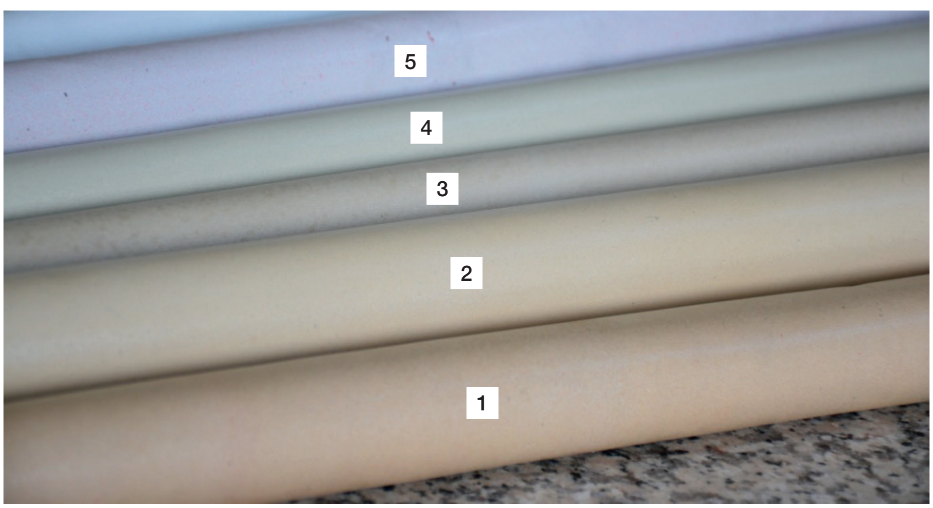

Figure 1. Color change observed in leather samples after finishing process
1- walnut shell; **2**- onion peel; **3**- oak bark; **4**- chemical pigment; **5**- water

Table VI

Dry rub fastness test results.

	Type of leather	Leather	Felt
Control	water 1	4	4
	water 2	4	4
	water 3	4	4
	chemical pigment 1	3/4	3/4
	chemical pigment 2	3/4	3/4
	chemical pigment 3	3/4	3/4
Experimental	walnut shell 1	4	4
	walnut shell 2	4	4
	walnut shell 3	4	4
	oak bark 1	4/5	4/5
	oak bark 2	4/5	4/5
	oak bark 3	4/5	4/5
	onion peel 1	4/5	4/5
	onion peel 2	4/5	4/5
	onion peel 3	4/5	4/5

Evaluation of dry rub fastness test results are shown in Table VII.

The results of evaluation of fastness to dry friction were higher in the experimental group. The tests were carried out three times. The leather treated with water instead of chemical pigment and the walnut shell showed a score of 4 three times. The leather treated with chemical pigment was rated at 3/4. Dry rub fastness of walnut shell higher than chemical pigment. Dry rub fastness was significantly higher in the oak bark and onion peel than chemical pigment, water and walnut shell and showed three times 4/5.

Wet rub fastness test results are shown in Table VIII.

Evaluation of wet rub fastness test results are shown in Table IX.

Even in a wet fastness test study, the experimental samples showed good results compared to the control sample. There were 4 score in the control group, exactly in water and chemical pigment. Onion peel and oak bark showed good results among herbal extracts, 4/5 score tree times. There were 4 in leather of walnut shell and 4/5 in felt.

Color measurement analysis results

Color measurements were evaluated according to the DE * ab (D65) results obtained from L * a * b color area measurements. Table X shows the results of color measurement evaluation.

In this study a*(D65), b*(D65), da*(D65), db*(D65) levels were considerably higher in the experimental group. There was considerably significant difference between control and experimental groups regarding to L*(D65), dL*(D65), dE*ab(D65) levels.

Table VII

Evaluation of dry rub fastness test results.

		Control		Experimental		
		water n(%)	chemical pigment n(%)	walnut shell n(%)	oak bark n(%)	onion peel n(%)
Leather	3/4	0 (0)	3 (100)	0 (0)	0 (0)	0 (0)
	4	3 (100)	0 (0)	3 (100)	0 (0)	0 (0)
	4/5	0 (0)	0 (0)	0 (0)	3 (100)	3 (100)
Felt	3/4	0 (0)	3 (100)	0 (0)	0 (0)	0 (0)
	4	3 (100)	0 (0)	3 (100)	0 (0)	0 (0)
	4/5	0 (0)	0 (0)	0 (0)	3 (100)	3 (100)

Table VIII

Wet rub fastness test results

	Type of leather	Leather	Felt
Control	water 1	4	4
	water 2	4	4
	water 3	4	4
	chemical pigment 1	4	4
	chemical pigment 2	4	4
	chemical pigment 3	4	4
Experimental	walnut shell 1	4	4/5
	walnut shell 2	4	4/5
	walnut shell 3	4	4/5
	oak bark 1	4/5	4/5
	oak bark 2	4/5	4/5
	oak bark 3	4/5	4/5
	onion peel 1	4/5	4/5
	onion peel 2	4/5	4/5
	onion peel 3	4/5	4/5

Table IX

Evaluation of wet fastness test results.

		Control		Experimental		
		water n(%)	**chemical pigment n(%)**	**walnut shell n(%)**	**oak bark n(%)**	**onion peel n(%)**
Leather	4	3 (100)	3 (100)	3 (100)	0 (0)	0 (0)
	4/5	0 (0)	0 (0)	0 (0)	3 (100)	3 (100)
Felt	4	3 (100)	3 (100)	0 (0)	0 (0)	0 (0)
	4/5	0 (0)	0 (0)	3 (100)	3 (100)	3 (100)

Table X

Evaluation results of color measurements

	Control		Experimental	
	Median (min-max)	**Ort+SD**	**Median (min-max)**	**Ort+SD**
L*(D65)	78.8(78.6/81.5)	79.7±0.57	69.9(69.1/74.9)	73.03 ±0.57
a*(D65)	-0.1 (-0.4 /-0.1)	-0.1±0.37	3.5(1.5/6.3)	3.8±0.38
b*(D65)	8.5(4.4/12.8)	8.58±0.19	24.4(15.8/37.7)	25.8±0.19
dL*(D65)	50.8(49.7/52.5)	50.8±0	41.1(40.2/-45.9)	44.15±0
da*(D65)	-0.01(-0.06/0.1)	-0.02±0.19	4.2(1.6/6.4)	3.94±0.19
db*(D65)	9(4.9/13.4)	9.2±0.38	24.7(16.2/38.3)	26.44±0.38
dE*ab(D65)	51.7(51.4/52.8)	51.8±0.57	52(48.3-59.9)	52.18±0.57

Table XI
Evaluation results of color measurements after aging process (24 hours)

	Control		Experimental	
	Median (min-max)	Ort+SD	Median (min-max)	Ort+SD
L*(D65)	78.5(78.5/80.3)	78.8±0.57	72(69.7/75.2)	72.5 ±0.57
a*(D65)	0.1 (-0.1 /0.8)	0.19±0.37	4(1.5/6.1)	4.01±0.38
b*(D65)	8.6(4.3/12.7)	8.6±0.19	25(15.7/37.9)	25.9±0.19
dL*(D65)	49.6(49.3/51.5)	49.9±0	43(40.8/-46.3)	43.64±0
da*(D65)	0.3(0.02/0.9)	0.3±0.19	4(1.6/6.2)	4.11±0.19
db*(D65)	9(4.9/13.3)	9.1±0.38	26(16.3/38.5)	26.57±0.38
dE*ab(D65)	51.7(49.6/51.7)	50.9±0.57	51(48.2-59.6)	51.77±0.57

Table XI shows evaluation results of color measurements after aging process under 60°C and 90% humidity conditions for 24 hours in a UV cabinet.

No significant difference was found between evaluation results of color measurements in Table X and Table XI in color.

Evaluation results of color measurements after aging process under 60°C and 90% humidity conditions for 96 hours in a UV cabinet are shown in Table XII.

Evaluation results of color measurements after aging process under 60°C and 90% humidity conditions for 96 hours in a UV cabinet showed that temperature and humidity did not negatively affect the color measurements of the leather.

Table XIII shows evaluation results of color measurements according to type of plants.

Color measurements of water and chemical pigment are almost the same. No significant difference was found between water and oak bark, walnut shell ($p < 0.01$). The dE*ab(D65) color value obtained in those using water was significantly lower than those onion peel ($p < 0.01$). Color measurements obtained by using onion peel were found to be significantly higher than chemical pigment ($p < 0.01$). There was no significant difference between chemical pigment and oak bark ($p < 0.01$). The dE*ab(D65) color value obtained in those using oak bark was significantly lower than those onion peel ($p < 0.01$). In our study, minor significant difference between walnut shell and oak bark color measurements. Delta E*ab(D65) color measurements were significantly higher in onion peel than walnut shell, oak bark. The results show that color measurements were minor significant difference between chemical pigment and oak bark. Color measurements were not significantly changed after the aging process of leather under 60°C and 90% humidity conditions for 24 and 96 hours.

Table XII
Evaluation results of color measurements after aging process (96 hours)

	Control		Experimental	
	Median (min-max)	Ort+SD	Median (min-max)	Ort+SD
L*(D65)	77.5(76.7/79.3)	77.8±0.57	73.9(69.1/75.7)	73.19 ±0.57
a*(D65)	0.5 (-0.1 /1.5)	0.5±0.37	3.7(1.7/6.3)	3.7±0.38
b*(D65)	9.2(5.1/13.0)	9.2±0.19	26(16.5/36.2)	25.6±0.19
dL*(D65)	49.1(47.9/50.4)	48.9±0	44(39.2/-47.5)	44.2±0
da*(D65)	0.5(-0.04/1.6)	0.6±0.19	4(1.9/6.4)	3.8±0.19
db*(D65)	9(5.7/13.6)	9.9±0.38	26(17.1/36.9)	26.24±0.38
dE*ab(D65)	50(48.3/52.2)	50.0±0.57	52(48.3-60.2)	51.95±0.57

Table XIII

Evaluation results of color measurements according to type of plants

		n	dE*ab(D65) Median (min-max)	Ort+SD	Test Value	p
Group	**Control**	**180**	50.7(50.5/51.5)	50.9±0.5	**25.16**	**a0.001****
	1. water	**30**	51.4(51.1/52.8)	51.8±0.7		
	2. water (24 hours)	**30**	50.2(49.6/51.7)	50.5±0		
	3. water (96 hours)	**30**	48.3(48.3/48.5)	48.4±0.7		
	4. chemical pigment	**30**	51.7(51.4/52.1)	51.8±0.57		
	5. chemical pigment (24 hours)	**30**	51.4(51.3/51.5)	51.4±0.57		
	6. chemical pigment (96 hours)	**30**	51.3(51.5/52.2)	51.7±0.57		
	Experiment	**270**	51.9(51.5/52.3)	51.9±0.28		
Plant extract	7. oak bark	**30**	48.3(47.8/48.7)	48.3± 0.52	**39.47**	**b0.001****
	8. oak bark (24 hours)	**30**	48.2(47.9/48.5)	48.3± 0.39		***Post Hoc;***
	9. oak bark (96 hours)	**30**	48.4(46.9/49.2)	48.2± 0.26		***1-4 p:0.001***
	10. onion peel	**30**	59.6(59.1/59.3)	59.5± 0.12		***1-7 p:0.001***
	11. onion peel (24 hours)	**30**	59.6(59.1/59.6)	59.4± 0		***1-10 p:0.001***
	12. onion peel (96 hours)	**30**	59 (58.9/60.2)	59.4± 0.13		***1-13 p:0.001***
	13. walnut shell	**30**	48.7(48.6/48.9)	48.7± 0.26		***4-7 p:0.001***
	14. walnut shell (24 hours)	**30**	47.5(47.4/48.1)	47.7± 0.39		***4-11 p:0.001***
	15. walnut shell (96 hours)	**30**	48.3(48.2/48.4)	48.3± 0.52		***4-15 p:0.001***

[a]Student t-test [b]Oneway Anova test&post hoc Bonferroni test **p<0.01

Conclusion

In this study, the possibility of using plant extracts as a dye in the finishing process of the leather was investigated. The recipe was provided according to the finished formula, replacing the chemical pigment with plant extracts, using oak bark, walnut shell and onion peel. For this reason, chrome-tanned crust leathers were dyed in the finishing process. These processes were repeated 3 times and compared with the control example of the leather, which is made according to the main recipe, where the chemical pigment and water were used. In these comparisons, visual evaluation, color measurement, dry and wet rubbing fastness were analyzed according to standard methods. The color measurement evaluation results showed that there was no significant difference between control and experimental groups regarding dE*ab (D65) levels.

According to the dry rub fastness test results, the experimental group showed excellent results, especially the leather finished by onion peel and oak bark extracts showed 4/5 score, when water and chemical pigment from control group were rated at 4 score. During the wet rubbing fastness, a good color quality was observed in the experimental group. The results of the study showed that in all experiments the experimental group showed a good result and plant extracts can be used as biocolorants during the finishing process. The finishing formulation used in this research belongs to the factory itself. The proportions of the materials used may vary according to the desired properties. For this reason, it may be appropriate to try plant extracts in different formulations.

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Evaluation of the Physical Properties of Goatskins Tanned using Banana (*Musa spp.*) Leaf Midrib Tannins

by

James K. Wangui,* Benson Ongarora and Douglas Onyancha
School of Science, Department of Chemistry, Dedan Kimathi University of Technology
Private Bag, Dedan Kimathi - Nyeri, Kenya.

Abstract

Vegetable tannins have been studied over the years with an aim to reduce the pollution load caused by chrome tanning. Although mimosa tannins have been utilized commercially, they are expensive and not readily available. The purpose of this study was to assess the physical properties of leather tanned with banana leaf midribs tannins in order to determine their suitability as vegetable tannins. Selected banana leaf midrib samples were collected from Gikondi village in Mukurweini, Nyeri County, Kenya. They were shade-dried and ground into powder. The skins were processed conventionally using banana leaf midribs tannins of *Musa sapientum Linn.* and 'Muraru' (AA genome), with mimosa as a control. The physical properties of the resultant leathers were determined following the standard IUP methods. It was found that *Musa sapenitum Linn*, 'Muraru' (AA genome) and mimosa-tanned leathers had average shrinkage temperatures of 80.33 ± 0.74°C, 78.67 ± 0.47°C and 81.67 ± 0.94°C, respectively. The properties of the tanned leathers were compared with those of the control-tanned leather. Assessment of the physical properties indicated that the leathers met the minimum recommended values safe for *Musa sapentium Linn*-tanned leather, which failed at 30,000 flexes. These results indicate that banana leaf midribs can be used as an organic tanning agent source for production of leathers from goatskins.

Introduction

The present market value of the leather industry worldwide is around US$50 billion.[1] However, majority of the hides and skins produced in Kenya, the sixth-largest raw material producer for the industry in the world, are exported. Notwithstanding, the industry plays a significant role in Kenya's economy by employing hundreds of citizens across the nation. Leather production involves the stabilization of collagen by crosslinking its fibers to prevent deterioration and increase its hydrothermal stability.[2] Vegetable-, chrome-, and aldehyde-tanning are the three most utilized tanning techniques.[3]

Vegetable tanning involves the use of plant polyphenols (also known as tannins) to stabilize the collagen against putrefaction. These tannins are categorized into condensed tannins and hydrolysable tannins.[4] Leathers produced using these polyphenols are usually firm, compact and flexible, making them suitable for production of sole leathers, upholstery and leather goods. Polyphenols have also been utilized in tanning and retannage as they offer a filling effect among other attributes as mentioned.[5] The modification is thought to be a result of the polyhydroxy groups bonding to the active chains of the polypeptides, especially the carboxylic chains, either by hydrogen bonding, ionic bonding or covalent bonding.[6]

Tannins may be acquired from galls, which are primarily present in plant branches and leaves, and form in response to insect and parasitic attacks. The tannins utilized during tanning are typically round-shaped, smooth, and contain tannin levels ranging from 40% to 70%.[7] Fruits form another source of tannins used in leather production. Valonia and dividivi trees provide fruit-derived tannins, which have been utilized in Australia, Germany, and France due to their ability to provide characteristics such as solidity and weight to leather. They are also linked to the production of leather that possesses a degree of water resistance.[8] Leather production using sumac leaves has been practiced, and these leaves reportedly contain approximately 25% tannins.[9] In the 19th century, quebracho was investigated and employed for leather production purposes.

Tree barks are the primary source of tannins, which typically contain tannin levels ranging from 6% to 17%. Oak tree barks have been conventionally utilized as vegetable tanning agents, and other types of tree barks, such as acacia, have also been used for this purpose.[10,11] Coffee grounds have equally been utilized to tan leather.[12] The use of tree barks from acacia, if not managed appropriately, could result in deforestation, which in turn could have adverse effects on global warming.[13] Therefore, there is need to explore alternative sustainable sources of vegetable tanning agents.

Banana farming is well established, ranking among the top five in the world. Production capacity is estimated at ninety million tons of this fruit among the tropical and sub-tropical regions like Africa, South and Central America and South Eastern Asia producing 13%, 28% and 47% respectively.[14] Banana cultivation occupies approximately 1.4 million hectares or 38% of agricultural land in Uganda, thus making it the most extensively grown crop.[15] It is also regarded as one of the key crops for ensuring food security in Central, Western, and Eastern Africa.[16] Bananas (*Musa spp*) are a staple food and a source

*Corresponding author: kiharawangui76@gmail.com
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of income to a large number of homesteads across East Africa. The region provides about half of the bananas sold in Africa.[17] In Kenya, the types of bananas grown are mainly the cooking and dessert varieties, and they are mostly grown in Central and Nyanza regions.[17] Their distribution is greatly influenced by feeding behavior, supply and demand ratio, local tastes and climatic conditions.[18]

Studies conducted on Kepok bananas (*Musa paradisiaca L.*) have shown that the tannin levels in the leaves, trunks, and peels of these bananas range from 3.7% to 5.5%, making them a potential source of vegetable tanning agents.[19] Banana leaf midrib (*Musa acuminata balbisianacolla*) has been estimated to contain tannins in the range of 12% to 16%.[20] *Musa sapentium Linn.* and 'Muraru' (AA genome) tannin contents were determined and found to be 11.71 ± 0.33% and 6.36 ± 0.19%, respectively.[21] This study is aimed at assessing the physical properties of the leathers produced using selected banana leaf midrib tannins (by comparing the results with set minimum standards) in order to determine their potential to substitute or supplement mimosa as a vegetable tanning agent. This will ensure sustainable source of plant tannins.

Experimental

Materials

Banana leaf midribs of *Musa sapientum Linn.* and 'Muraru' (AA genome) were collected from Gikondi village in Mukurweini, Nyeri County. Powders were prepared following a procedure published in the literature.[21] Wet salted goatskins were purchased from a local slaughterhouse in Nyeri, Kenya. Mimosa was purchased from Sagana Tanners Limited and all the other chemicals used during the leather processing were purchased from Priyann Industries. The chemicals used were of reagent grade.

Tanning process

The sets of skin were weighed and treated through the same beamhouse processes and separated into three groups at the tanning stage. During beamhouse treatment, soaking was carried out using 300% (weight/weight) water, 1% wetting agent, and 0.01% fungicide for 24 hours. Then paste-liming was done to unhair the goatskins using 20% water, 8% lime and 2% sodium sulfide. The paste was applied on the flesh side of the skins, folded and then left to stand overnight. The unhaired skins were then relimed with 200% water, 5% lime and 0.05% sodium sulfide for 24 hours and the pH was checked. The liquor was drained, skins washed and liquor drained again. The pelts were then fleshed. Before deliming, the pelts were weighed. Deliming was carried out with 150% water and 2% ammonium sulfate and run for one hour and then the pH was checked. 1% bating enzyme was added and the process run for another hour. Thumb test was performed to confirm the completion of the bating process.

The goatskins were treated with extracts from two different types of bananas, and with mimosa as the control tanning agent. In three separate drums, pre-tanning was done using 100% water and 1% glutaraldehyde for two hours.[19] Moreover, for the control, 30% mimosa powder was added in four batches as shown in Table I and for the experimental leathers, 40% of the selected powdered banana leaf midribs were added in five batches as shown in Table II.[22,23] Penetration was confirmed by cutting a cross-section at the neck region of the pelts. The process was continued until the tannages were complete and the tanning liquors in the three drums were exhausted. Then, formic acid (1%) diluted with water at a ratio of 1:10 (volume by volume) was added in two steps and the process was run for two hours. The pH was measured. The leathers were drained, washed, and left to age overnight. Fatliquoring was done with 100%

Table I
Process recipe for Mimosa tanning

Process	Chemical	Percentages (%)	Duration (hours)	Remarks
Pre tanning	Water	150		
	Glutaraldehyde	2	2	
Tanning	Mimosa	5	24	Check penetration
		5	24	pH 5.0
		10	24	
		10	24	
Fixing	Formic acid	1	2	pH 3.5
Drain, wash and drain. Leave Overnight for aging				
Fatliquoring	Sulfated fatliquor	3	2	
	Sulfited fatliquor	3		
Fixing	Formic acid	1	2	
Drain, wash and drain. Horse overnight. Toggle dry				

Table II
Process recipe for banana leaf midrib tanning

Process	Chemical	Percentages (%)	Duration (hours)	Remarks
Pre tanning	Water	150	2	
	Glutaraldehyde	2		
Tanning	Banana (*Musa spp*) leaf midrib powders	5	24	Check penetration
		5	24	pH 5.0
		10	24	
		10	48	
		10	48	
Fixing	Formic acid	1	2	pH 3.5
Drain, wash and drain. Leave Overnight for aging				
Fatliquoring	Sulfated fatliquor	3	2	
	Sulfited fatliquor	3		
Fixing	Formic acid	1	2	
Drain, wash and drain. Horse overnight. Toggle dry				

water at 35°C, 3% sulfated fatliquor, and 3% sulfited fatliquor for two hours, before being fixed with 1% formic acid. The leathers were horsed overnight and then toggle dried.

Physical Testing

Sampling and sample preparation

The samples were cut as per the standard official method specified under IUP 2 (2001) in triplicates, both transversely and longitudinally towards the backbone, for all the physical tests. The samples were then conditioned at a standard atmosphere of 20 ± 2°C temperature and 65 ± 4% relative humidity for more than 24 hours according to IUP 3 (2001).

Determination of shrinkage temperature

Shrinkage temperature was determined in accordance with IUP 16 (2001). The leather samples were cut into strips of 50 mm by 2 mm for parallel and perpendicular specimens and suspended over a heating media in a water jar. The temperature at which significant shrinkage was seen was recorded as the leather's shrinkage temperature.

Mechanical analysis of the tanned leathers

All tests were carried out in triplicate for both the parallel and perpendicular runs. Tensile strength was determined using an Instron machine 1026 in accordance with IUP 6 (2001). The samples were clamped on a pair of jaws separated at a height of 50 mm. The maximum force exerted to break the specimens was recorded as the tensile strength and expressed in N/mm^2. Tear strength was recorded as per IUP 8 (2001) on an Instron machine 1026. Specimen samples of 50 mm by 25 mm were clamped on a pair of holders secured on the machine. The highest force exerted to cause tear was recorded as the tear strength and expressed in Newtons (N). Ball burst extension was demonstrated using disc-shaped samples of 44.5 mm diameter. The samples were placed on a machine with the grain side up and the flesh side touching the tip of the steel rod. Bursting and cracking of the grain surface were noted and expressed in millimeters (mm). A bally flexometer machine was used to test the number of flexes the leather would endure before failure.

Results and Discussion

Tanning

This stage was preceded with beamhouse operations. Among other operations, hair, fats and flesh were removed to ready the material for tanning operation. Reliming was done to facilitate the opening up of the fibers and removal of any residual hair debris left on the skins. Glutaraldehyde was used as a pretanning agent before vegetable tanning to help aid in more firm leather as well as act as a penetrating agent to better the tanning process. On treating the pre-tanned goatskins with extracts from the two different species of bananas and mimosa powder as the control tanning agent, the leathers obtained showed differences in their physical and organoleptic properties as shown in Figure 1 (a-f). The banana leaf midrib powders required a longer time to fully penetrate the skin matrix compared to the mimosa powder. This difference in penetration time could be due to various factors, such as the varying molecular size of the tannins, tanning strength of the tannins (which were 1.61, 1.82 and 2.07 for 'Muraru' (AA genome), *Musa sapentium Linn.* and mimosa powders, respectively) and pH of the tanning solutions used, as well as differences in the chemical structure of the tannins themselves.[21]

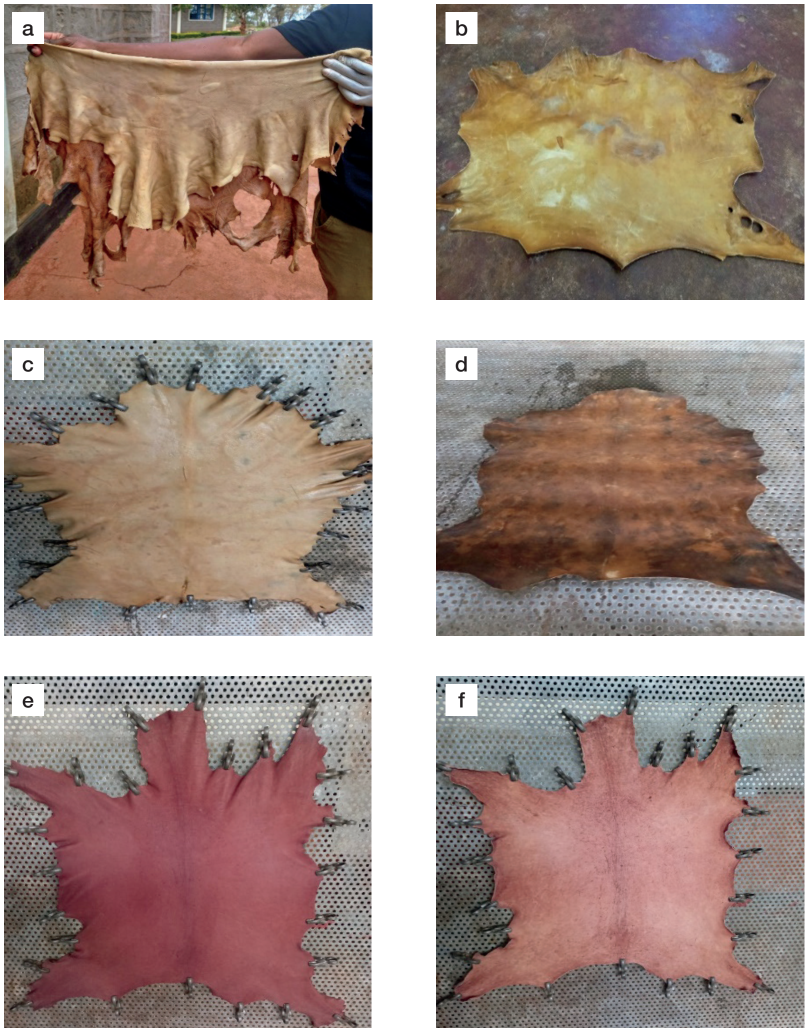

Figure 1. Leathers obtained from different tannages:
Muraru (AA genome)-tanned wet **(a)** and dry **(b)**;
Musa sapentium Linn.-tanned wet **(c)** and dry **(d)**;
mimosa-tanned wet **(e)** and dry **(f)** leathers

The wet and dried leathers showed color variations. This could be attributed to the aromatic compounds in the tannins that cause them to change color when exposed to light due to the formation of quinones on the tannins.[24]

The formation of free radicals causes rearrangement of chemical bonds and coupling of oxidized molecules, resulting in the formation of polymeric materials. If this process leads to the formation or linking of chromophoric groups, then color develops.[6] However, hydrolysable tannins have chromophores that cannot be linked together because they are located too far apart within the molecule. This results in the tannins being resistant to reddening and they are, therefore, considered to be light-fast.[25] The selected banana leaf midrib tanning agents are of condensed type,[21] and hence are affected by this effect because in the flavonoid structure, the aromatic nuclei are close together, making it easier for free radical oxidative bond rearrangements to occur.[6] This made the surfaces of the leathers quickly change their color. As a result of these tannins, reddening can be seen within Figure 1(b) and 1(d).

Physical Properties of the tanned leathers

The mean values of the physical tests of the leathers tanned with *Musa sapentium Linn*., 'Muraru' (AA genome) and the control commercial tanning agent mimosa are as shown in Table III below.

Shrinkage Temperature

The mimosa-, *Musa sapentium Linn*.- and 'Muraru' (AA genome)-tanned leathers had values of 81.67 ± 0.94°C, 80.33 ± 0.94°C% and 78.67 ± 0.47°C, respectively. All the tanned leathers had shrinkage temperatures above the accepted value of 75°C.[26] Shrinkage temperatures above the minimum recommended value imply that the organic agent and the collagen matrix have formed strong

Table III

Physical Properties of Selected banana leaf midrib tanned leathers and Mimosa tanned leather

Physical properties		**Mimosa**	***Musa sapentium Linn.***	**'Muraru' (AA genome)**	**Minimum recommended value**
Shrinkage temperature (°C)		81.67 ± 0.94	80.33 ± 0.94	78.67 ± 0.47	>75
Tensile strength (N/mm2)	↑	16.54 ± 0.79	15.79 ± 0.31	20.54 ± 0.88	>12
	→	15.21 ± 0.46	13.16 ± 0.46	17.19 ± 0.41	
Tear strength (N/mm)	↑	51.61 ± 0.62	46.66 ± 0.95	40.37 ± 0.90	>20
	→	52.82 ± 0.39	59.16 ± 0.26	45.29 ± 0.74	
Percent elongation (%)	↑	43.53 ± 3.18	50.60 ± 2.95	61.10 ± 2.14	>40
	→	38.13 ± 0.74	32.67 ± 3.37	60.00 ± 2.29	
Ball burst extension (mm)	Grain crack	7.57 ± 0.22	6.86 ± 0.18	8.19 ± 0.33	6.50
	Ball Burst	8.72 ± 0.19	7.82 ± 0.46	10.22 ± 0.46	7.00
Thickness (mm)		2.10 ± 0.60	0.93 ± 0.05	0.77 ± 0.05	0.50
Flexing endurance (flexes)		No damage @50,000	Damage @30,000	No damage @50,000	50,000

crosslinks.[23] The selected banana midrib-tanned leathers had higher values in comparison with studies done by Maryati *et al*., (2020) on banana bunch tanning of rabbits skins, where the shrinkage temperature was found to be 52.47 ± 4.27°C.[27] Mimosa-tanned leather shrinkage temperature was close with studies done by Tanui *et al*., (2019), where it was reported that mimosa-tanned rabbit skins to have a shrinkage temperature of 83°C.[28]

Tensile Strength

Longitudinally, 'Muraru'-tanned leather had the highest tensile strength of 20.54 ± 0.88 N/mm^2, while *Musa sapentium Linn*.-tanned leather had the lowest value at 15.79 ± 0.31 N/mm^2. A significant difference ($p < .05$) in tensile strength was found longitudinally between 'Muraru' (AA genome)-tanned leather and mimosa-tanned leather, however no significant difference ($p > .05$) was observed between *Musa sapentium Linn*.-tanned leather and mimosa-tanned leather. Transversely, 'Muraru'-tanned leather had a tensile strength of 17.19 ± 0.41 N/mm^2, while *Musa sapentium Linn*. tanned leather had 13.16 ± 0.46 N/mm^2. No significant difference ($p > .05$) was found between 'Muraru'-tanned leather and mimosa-tanned leather, or between *Musa sapentium Linn*. and mimosa-tanned leather. All three tanning agents used exceeded the minimum recommended value of 12 N/mm^2.[26] The study findings indicate that samples cut perpendicular to the backbone had lower strength compared with those cut longitudinally and this is as a result of greater damage to the fibers resulting from increased friction, which occurs due to their alignment.[28]

The strength of leather is determined by the modification of the collagen fibrils caused by crosslinking with tanning agents. It is defined as the maximum amount of stress it can endure in the longitudinal direction without breaking.[9] Little has been done on tannin of goatskins with banana tannins. These values were lower compared to studies carried out using kepok banana bunch tannins, where the tensile strength of the tanned rabbit skins was found to be 29.61 N/mm^2.[19] The variation in tensile strength between the selected banana species tanning agents was associated with the variation in thickness which occurred as a result of an increased plumping effect in the *Musa sapentium Linn*.-tanned leather due to the low acid and salt content of its tanning liquor.[9] This swelling effect also increases the weave angle due to the increased distance between the collagen fibers reducing the load transfer hence resulting to lower strength.[29] The obtained values for mimosa-tanned leather closely matched with literature values.[2,30] It is worth noting that tensile strength is greater near the backbone compared to further away from it, which can be attributed to the way the fibers are arranged and packed.[31]

Tear strength

Tear strength values for specimens cut parallel and perpendicular to the backbone of mimosa-, *Musa sapientium Linn*.- and 'Muraru' (AA genome)-tanned leathers were found to be significantly different ($p < .05$). Parallel specimens of mimosa, *Musa sapientium L.* and 'Muraru' (AA genome) tanned leathers had values of 51.61 ± 0.62, 46.66 ± 0.95 and 40.37 ± 0.90 N/mm respectively. Perpendicular specimens had values of 52.82 ± 0.39, 59.16 ± 0.26 and 45.29 ±

0.74 N/mm respectively. Likewise, for samples cut perpendicular to the backbone, there was a statistical difference in all the tanned leathers ($p < .05$). All of the vegetable-tanned leathers examined in this investigation had tearing strengths greater than 20 N.[26] Studies done by Oliveira *et al.,* reported similar results for tear strength (58.9 N) for goatskins.[32] According to research done in Kenya using Acacia tannin extracts, goatskin samples of *Acacia nilotica* had 42 N, *Hagenia abyssinica* had 31 N, *Acacia xanthophloea* had 34.92 N, and *Acacia mearnsii* extract had 34.22 N.[9]

Grain crack and Ball burst

Grain crack values for mimosa, 'Muraru' and *Musa sapentium Linn*. tanned leathers were 7.57 ± 0.22 mm, 8.19 ± 0.33 mm and 6.86 ± 0.18 mm respectively. Ball burst values for mimosa, 'Muraru' and *Musa sapentium Linn.* -tanned leathers were 8.72 ± 0.19 mm, 10.22 ± 0.46mm and 7.82 ± 0.46 mm respectively. Grain crack comparisons between mimosa, 'Muraru' (AA genome) and *Musa sapentium Linn.* -tanned leathers revealed no statistically significant difference between mimosa and 'Muraru' ($p > .05$). However, there was a statistically significant difference between mimosa- and *Musa sapentium Linn.*-tanned leathers ($p < .05$). Ball burst comparison between mimosa-, 'Muraru'- and *Musa sapentium Linn.*-tanned leathers showed no significant difference ($p > .05$). The ball burst test is an important measure of the strength of upper leathers in shoe manufacturing, expressed in millimeters. It assesses the leather's resistance to cracking when it is lasted during shoe production. Grain crack and ball burst minimum recommended values are 6.5 mm and 7.0 mm, respectively.[26] Studies done in Kenya on *Plectranthus barbatus* indicated that mimosa-tanned leather had 7.7 mm and 8.2 mm values for grain crack and ball burst respectively, this did not differ much with our findings.[9] This was also in agreement with a study conducted using coffee pulp tannins, which reported 7.47 ± 0.09 mm and 8.25 ± 0.15 mm for grain crack and ball burst for mimosa-tanned leathers.[31] The greater the softness in the leather is attained the higher the busting height.[33]

Flexing endurance

Leathers from mimosa and 'Muraru' (AA genome) tannins had the highest flexion and bending capabilities, withstanding up to 50,000 flexes. Leather tanned from *Musa sapentium Linn*., however, was not able to withstand the same amount of flexes. It could only be able to hold up to 30,000 flexes. The failure was attributed to the firmness of the leather, hence being rigid in undergoing flexing. *Musa sapentium Linn.*-tanned leather may be used to make leathers for harness and saddlery and furniture as the leathers do not undergo much flexing during use with a minimum recommended value of 20,000 flexes.[26] Flexing endurance is carried out to tests finishes on leather surfaces as well as a fastness test in light leathers.[34] It is an assessment of leather's crack resistance during continuous flexing.[35] As shoes require materials with high and compatible flexion and bending capabilities, leather materials are subjected to this test to determine if it is suitable for this application. Research carried out on three types of Nigerian goats that were tanned using *Acacia nilotica* tannins did not reveal any significant variation in flexibility. Out of all the samples taken, only 5.83% displayed surface cracks on the leather.[36] Studies conducted on leathers that were tanned using Sunt pods, pomegranate husk, and mango leaves found that the leathers could endure up to 30,000 flexes without developing any cracks.[30]

Conclusion

The research findings from this study show that tannins derived from banana midribs can be employed as a substitute tanning agent for goatskins. Results showed statistical differences in some of the physical properties assessed, yet all the tests yielded values that surpassed the minimum set requirements for good quality leathers except for flexing endurance where *Musa sapentium Linn.*-tanned leather could only be able to hold up to 30,000 flexes. It was noted that leather samples cut along the backbone generally had superior properties as opposed to those cut across the backbone. This difference is thought to be due to the anisotropic nature of the hide and skin structure. As such, selected banana midrib tannins can be used to produce light vegetable-tanned leathers. To expand on these findings, future investigations should explore the use of banana leaf midrib tanning on other raw materials, such as sheep and exotic skins, either alone or in combined tannages.

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Effect of Pigment-Acrylic Binder Ratio on the Surface and Physical Properties of Resin Finished Leather

by

Suriya Madhan,[a] Mishamo Wakaso,[b] Sathya Ramalingam[a] and Swarna V Kanth[a*]

[a]*CSIR-Central Leather Research Institute*, Adyar, Chennai- 600020, India.

[b]*Leather Industry Development Institute*, Ethiopia.

Abstract

The current study attempts to investigate the surface phenomenon and physical characteristics of leather finished with brown pigment and different types of acrylic binders. Using the contact angle measurements of three different liquids on the above finished leathers and films, the surface energy and work of adhesion were evaluated. The pigment to acrylic binder ratio (PABR) for best adhesion of finish film on the leather surface was optimized using the contact angle goniometer. Different types of acrylic binder films were coated and their surface behaviour was studied. The crust leather was coated with different types of pigment-acrylic binder (Very Soft, Soft and Medium Soft) finish formulations. The contact angle of both the acrylic films and the PABR finished leathers were measured against Water, Dimethyl sulfoxide (DMSO) and Hexadecane (HD). According to the study's results, the surface properties of finished leather were directly related to the degree of wetting. The PABR was found to be effective at 1:3 for very soft binder, 1:2.5 for soft, 1:2 for medium soft binders due to higher contact angle and lower surface energy values (γsv). At 1:3 and 1:2.5, the contact angle of very soft and soft binder leather was 82.62° and 83.45° and for medium soft binder it was 82.67° at 1:2 ratio. The surface energy values of optimized PABR of very soft binder (1:3) was 28.29 (mN/M), soft binder (1:2.5) was 27.50 (mN/m) and medium soft binder (1:2) was 29.27 (mN/m). The optimized PABR work of adhesion values of very soft binder, soft binder and medium soft binder was 82.15 (mJm^{-2}), 81.11 (mJm^{-2}), 82.09 (mJm^{-2}). In order to correlate the observed surface properties with leather finish properties, finished leathers were tested for finish adhesion, vamp flexing value, water vapour permeability, wet and dry rub fastness. According to the water vapour permeability, soft and medium binder showed good permeation due to the uncovering of nanopores. But the adhesion, grain crack resistance and grain smoothness were higher in the case of the soft binder. Overall leather properties divulges that the pigment to binder ratio and the type of binder plays an important role in surface properties of the finished leather. This study enables us to determine the optimal PABR for effective finish properties to meet the required leather standards for various usage, as well as better utilisation of finishing chemicals.

Introduction

Leather finishing is an essential process in leather production as it possesses a significant impact on the final appearance and performance of the leather product.[1] The finishing process not only gives a finished and aesthetic look, but also protects and adds value to it.[2] The finishing process increases the surface properties and resistance to mechanical stress such as bending, scuff resistance, wet and dry rub fastness by coating with acrylic, polyurethane (PU), butadiene, and other additives. The finishing process improves the quality of leather by minimising surface imperfections.[3] The finishing materials, methods and procedures might vary the texture, appearance, gloss and surface of the finished leather products. The constituents of leather finishing are pigments, dyes, acrylic binders, PU, protein binders, wax, emulsions, fillers etc. in the base coat with lacquer and lacquer emulsion at the top coat. Silicone and wax emulsions are also used as feel modifiers. Many acrylics, PU, and butadiene resin binders are used in the leather finishing process to generate films that improve the leather's resistance to moisture as well as its look and surface characteristics. These binders are macromolecular compounds with film-forming capability that holds the substrate together i.e., pigment and other chemicals used in leather finishing.[4] The pigment quality depends upon the degree of dispersion and particle size. Inorganic and organic pigments are used.[5] The covering power of organic pigments is less than that of inorganic pigments.[6] Pigment Volume Concentration (PVC) is the ratio of pigment volume divided by the sum of pigment and binder volume. Pigment Volume Concentration = Pigment volume / (Pigment + Binder volume). Excessive use of binder affects the adhesion, flexibility, and aesthetic look of leather and also enhances the cost of the finishing process.

Surface properties of the finished leather will vary based on the nature of the crust leather, mechanical operations and finishing auxiliaries. The surface related parameters of finished leathers were characterized based on the surface energy, work of adhesion and wettability on different solvents. Surface charge of the leather was strongly influenced by the penetration and fixation of chemicals in leather.[7] The resin binders (acrylic/PU/butadiene) significantly contribute to the charge of the finished film. The charge of the final leather acquiring a positive or negative charge depends on the quality

*Corresponding author email: swarna@clri.res.in

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Table I

Characteristics of the binder chosen for finishing application

Binder	Glass transition temperature (Tg, °C)	Mean Diameter (nm)	Solid contents %
Very soft acrylic binder	-34	96.1 ± 4	20-25
Soft acrylic binder	-30	101.7 ± 3	24-30
Medium soft acrylic binder	-27	120.3 ± 2	28-36

and quantity of the type of acrylic binders used.[8] Acrylic binders used for finishing are usually amphoteric. The water solubilising group of carboxyl, when reacted to the surface converts into an anion. The reliability of the finishing chemicals influences the physical performance of the finishes. The surface charge, surface tension and liquid–solid contact angle influences the wetting, penetration and spreading.[9-10] Water vapor permeability is the ability of moisture to penetrate through it. The adhesive strength and rub fastness are affected by a good finish.[11] It is one of the most essential physical properties of leather, which might lower permeability by adding binders. The finishing materials and process were chosen based on the leather's condition, the type of finish to be made, and the desired quality of the waterproof finished leather.[12-13]

In the present paper, different finishing formulations were prepared by varying the ratio of pigment and binder concentrations. Different finish films and finished leathers were prepared from various finish formulations. The study correlates the film forming properties of the finish formulations. Through the work, the optimum pigment to binder ratio was determined, which helps in the utilization of the exact amount of chemicals in the finishing process to qualify for the standards specified for varied leathers. It helps us to understand the surface morphology of leather finished using different pigment to binder combinations.

Materials and Method

Materials

In order to produce the dyed crust leather for the finishing process, the post tanning operations of wet blue leather from goat skins were carried out by using the conventional post tanning process. Similar grades of leather were used in the experiments.

Different finishing chemicals used in the finishing formulations were purchased from Stahl India, a leather chemical manufacturing company. The finishing chemicals used for the current study are acrylic based resin binders (very soft, medium soft, soft), pigment, wax emulsion, protein binder, filler and water. According to the T_g (Glass transition temperature), binders are classified as very soft, medium soft, and soft for experimental work. According to Winter et al., the lower the T_g value, the softer the polymer.[14] The T_g of the very soft binder was found to be -34°C, while the T_g of the medium soft binder was -27°C.

Method

Finish Formulation Preparation

Different finishing formulations were prepared by keeping the pigment and other auxiliaries constant and varying the concentrations of Very soft (VS), Soft and Medium soft (MS) binder as given in Table II.

Table II

Finish Formulations Prepared at a Varied Concentration of different Acrylic Binder

Finishing Chemicals	Quantity (ml)					
Pigment	100	100	100	100	100	100
Resin binder@	50	100	150	200	250	300
Filler wax	30	30	30	30	30	30
Protein	30	30	30	30	30	30
Water	790	740	690	640	590	540
Total	1000	1000	1000	1000	1000	1000

The above finish season was applied on the dyed crust leathers with roller coater equipment for control and respective experimental leathers. 4 coats were given for all the samples with an intermediate hydraulic press using a plain plate. The unlacquered leathers were taken for measurement.

@ – Soft, medium soft and very soft binders were used.

Finished Upper Leather Preparation

Thirty pieces of Goat shoe upper black dyed crust leather in the range of 4-5 Sq. ft. were used to study the effect of pigment to binder ratio in the finishing process. The thickness of the crust was uniformly maintained at 1 mm. The finish formulations as given in Table II were used for the finishing process. Leathers with varied formulations of Pigment-Binders were denoted as ‘F’. The formulation codes based on the quantity and nature of the binder were named as

FVS1 (25ml); FVS2(50ml); FVS3(75ml); FVS4(100ml); FVS5(125ml); FVS6(150ml) for very soft binder

FS1 (25ml); FS2(50ml); FS3(75ml); FS4(100ml); FS5(125ml); FS6(150ml) for soft binder

FMS1 (25ml); FMS2(50ml); FMS3(75ml); FMS4(100ml); FMS5(125ml); FMS6 (150ml) for medium soft binder

Acrylic Binder Film Preparation

Finish films were prepared on glass plates measuring 10×5×0.5 cm as per the formulations shown in Table II. The acrylic finish formulations (25 ml) were taken on the glass plates and allowed to dry at 60°C. The film-forming properties and physical properties of acrylic binder films were investigated.

Determination of Contact Angle

The contact angle of various solvents on acrylic binder films, dyed crust leather, and finished leather were measured using an ACAM contact angle instrument. Water, DMSO and hexadecane were the solvents used for the contact angle measurements. It is the quantitative measure of the wetting of solid (leather/film) by liquid. The interfaced tensions between solid liquid (SL), liquid vapor (LV), and solid vapor (SV) which occur when a drop of liquid is resting on a solid surface like leather/film and creating a contact angle, may be defined as the drop being in equilibrium while it is at rest.

Measurement of Work of Adhesion

The work of adhesion can be defined from Young’s equation and Young-Dupre relation, $Wa = \gamma LV (1+ \cos\theta)$, where Wa is the work of adhesion that was measured using θ, the angle in the contact angle (degrees).[7]

Measurement of Adhesion of Finish

The adhesion force of finished leather was measured according to IUF 470.[15] Samples from all the crust and finished leathers of 5×14 cm were cut from the official sampling positions of the leathers.

Determination of Flexing Endurance

Measurement of the Flexing resistance of finished leathers was carried out by IUP 39[16] from samples of crust and finished leathers that were cut from the official sampling positions of the leathers.

Determination of Wet and Dry Rub Fastness

Measurement of Wet and Dry rub fastness test of finished leathers was carried out according to IUF 450.[17]

Determination of Water-Vapor Permeability

The Water vapor permeability of the finished leathers was measured according to IUP 15.[18]

Determination of Physical Strength Characteristics

The various strength characteristics such as tensile strength and elongation at break were measured as per IUP 6,[19] and tear strength as per IUP 8.[20]

Determination of Organoleptic Properties

The organoleptic properties enable us to assess the quality of leather produced for diverse applications such as fullness, smoothness, grain smoothness, grain fullness, and color. The leathers were scored from 0-10, having higher ratings indicating superior properties, according to the evaluation of experts.

Results and Discussion

The surface charge of the crust leather to be finished and the finish formulations of a particular type of leather determine the final properties, characteristics, and surface behaviour of the final leather. The finishing chemicals play a significant role in improving the surface properties (like fullness, covering and grain smoothness) and reducing the anisotropic property with respect to the feel of the finish in the final leather. There are a wide variety of acrylic binders that influence the functional surface properties of the leather. It is of prime importance to know how each of the acrylic binders behaves in influencing the surface characteristics of leather with respect to its charge, surface energy and work of adhesion. Using Young’s equation, the surface free energy of the acrylic films, crust and finished leather was calculated from the contact angle values as given below in equations 1 to 8.

$$\gamma lv(1+\cos\theta) = 2[\sqrt{\gamma sv^{d}\gamma lv^{d}} + \sqrt{\gamma sv^{p}}\sqrt{\gamma lv^{p}}] \quad (1)$$

Where θ is the contact angle

γlv = liquid- vapor surface energy

γsv^{d} = solid- vapor interfacial energy of non-polar component

γlv^{d} = liquid- vapor interfacial tension of non-polar solvent

γsv^{P} = solid- vapor interfacial energy of polar component

γlv^{P} = liquid- vapor interfacial energy of the polar component

In the case of non-polar component, the polar component will vanish.

$$\gamma lv(1+\cos\theta) = 2[\sqrt{\gamma sv^{d}\gamma lv^{d}}] \quad (2)$$

Substitute the non-polar component in equation 1. The polar component was calculated using equation 3.

$$\gamma lv(1+\cos\theta) = 2[\sqrt{\gamma sv^{d}\gamma lv^{d}} + \sqrt{\gamma sv^{p}}\sqrt{\gamma lv^{p}}] \quad (3)$$

The total surface energy of the crust leather is the sum of both polar and non-polar components.

$$\gamma sv = \gamma sv^{p} + \gamma sv^{d} \tag{4}$$

Van Oss- Chaudhury- Good (OCG) thermodynamic approach can also be used to determine the surface free energy components of solids.[21-22]

In the current study, the polar component of surface energy, is expressed in the form of two components i.e., Lewis's acid and Lewis's base (γs^{+} and γs^{-}) parameters respectively.[23] To calculate these values in these experiments, three liquids such as water, DMSO and hexadecane were used.

$$\gamma lv(1+cos\theta) = 2\sqrt{\gamma s^{LW}\gamma l^{LW}} + 2\sqrt{\gamma s^{+}\gamma l^{-}} + 2\sqrt{\gamma l^{-}\gamma s^{+}} \tag{5}$$

For the non-polar component, the polar component in equation 5 was reduced to:

$$\gamma lv(1+cos\theta) = 2\sqrt{\gamma s^{LW}\gamma l^{LW}} \tag{6}$$

By substituting the known values non-polar components were calculated.

To calculate the Lewis acid parameter or the cationic nature of the surface, one can use polar and moderately polar contact angles and surface tension values. Since moderately polar was very small value compared to the polar value, it is neglected in equation 5 and the equation is reduced to

$$\gamma l(1+cos\theta) = 2[\sqrt{\gamma s^{LW}\gamma l^{LW}} + 2\sqrt{\gamma s^{+}\gamma l} \tag{7}$$

By substituting Lewis's acid parameter in equation 5, Lewis's base parameters were calculated.

The total surface energy is the sum of polar and non-polar components.[24]

$$\gamma s^{total} = \gamma s^{LW} + \gamma s^{P} \tag{8}$$

For the black dyed crust leather, contact angle values were measured at several regions such as the butt, backbone, neck, shank and belly. The contact angle values for the different regions of the leather were 78.42°, 73.47°, 69.01°, 66.02° and 62.43° for polar solvent (water). Due to spontaneous dispersion on the leather surface, measuring the contact angle value for moderately polar and non-polar solvents for crust leather is negligible. According to the above values, the butt region has the highest contact angle, while the belly region has the lowest. It was also found that each region of the crust shows a different value. In order to reduce the anisotrophicity of finish values in acrylic finished leathers, acrylic finish films were cast and placed on microscopic slides. The surface energy and work of adhesion were calculated using the contact angle values.

Contact Angle and Surface Energy and Work of Adhesion Parameters of different Acrylic Binder Films

The surface related parameters viz., surface energy and work of adhesion of very soft, soft, medium soft and hard binders were calculated based on the contact angle values for the films cast on the glass plates made with different liquids, viz., water, DMSO and hexadecane.

The contact angle values of polar solvent (water) showed an increasing trend from 60.23° to 87.75° for four different binder films in the trend, medium soft acrylic binder < soft acrylic binder < very soft acrylic binder < very hard acrylic binder. The higher contact angle values for hard binders indicate a non-smooth discontinuous film being formed. Hence, the hard binder cannot be used for the base coat, where film formation is completely not possible. The hard binder is used for specific finished leathers like crackle finish. Resin binders with smaller water contact angles were ideal for base coat because they spread quickly across the surface of the leather, which in turn facilitates the degree of adhesion.

The contact angle values of moderately-polar solvent (DMSO) showed a different trend, which can be attributed due to the nature of the monomers present and the behaviour of the acrylic polymer in presence of solvents in the binder film. The values for this moderately polar solvent ranged from 25.31° to 57.30° in the trend, very soft acrylic binder < very hard acrylic binder < medium soft acrylic binder < soft acrylic binder. For non-polar solvents, the values ranged from 7.80° to 20.54° in the trend, soft acrylic binder < medium soft acrylic binder < very soft acrylic binder < very hard acrylic binder. For leather finishing, the contact angle values of polar solvent are predominant, hence it is used for the entire finish film study for leather finishing.

The total surface energy value of a very hard acrylic binder is low in comparison to the other binders. The polar part of the surface energy (γsv^{p}) is very low for the hard binder and hence it does not form a continuous film. Comparatively, the surface energy values of the other three binders were greater, indicating that they had better adhesive qualities. It can also be seen that the difference between polar and dispersive surface energy values follows the trend of very soft binder (17.83 m/Nm) > soft binder (11.76 m/Nm) > medium soft binder (9.33 m/Nm). This indicates that the adhesion of the finish to the leather will follow a similar trend. However, we observed that the total surface energy values follow a reverse trend in comparison to the difference in polar and dispersive values. Hence, it can be concluded that the total surface energy is higher for very soft binders and hence, it binds better to the leather surface and requires more energy to remove the finish from the leather when compared to the very hard acrylic binder.

Table III

Contact Angle and Surface Energy and Work of Adhesion Value for Binders coated on a Microscopic Slide

S. No	Chemical name	Contact Angle (degree)			Surface Energy (m/Nm)			Work of Adhesion (mJm^{-2})		
		Water	DMSO	HD	γsv^d	γsv^p	γsv	Water	DMSO	HD
1	Very Hard Acrylic Binder	87.75	26.79	20.54	25.75	3.93	28.69	75.65	83.28	53.19
2	Very soft Binder	64.96	25.31	10.92	26.98	9.16	41.27	103.62	83.78	54.44
3	Soft Acrylic Binder	63.89	57.3	7.80	27.22	15.46	42.68	104.84	67.77	54.68
4	Medium Soft Acrylic Binder	60.23	50.6	8.65	27.16	17.83	44.99	108.95	71.93	54.63

Correlation between Surface Energy and Work of Adhesion Parameters for various PABR of Very Soft Binder

Based on the results from Table III, a separate set of experiments were carried out to assess the surface energy and work of adhesion of individual binders in combination with other chemicals like pigments, fillers, wax emulsion, protein binder and water added to the finish season for finishing of leathers. The experiment was conducted to understand the binding capacity of the acrylic binder to the pigment particles. The surface contact angle for different pigment binder ratios (@1:0.5 to 1:4) (PABR) of very soft binders were evaluated. The other finishing chemicals such as fillers, wax emulsion, protein binder, and water were kept constant along with pigment and the resin binder concentration alone was varied based on the PABR. The leathers were finished and the values for surface energy and work of adhesion are reported in Table IV.

The surface contact angle of leathers finished with varied PABR of very soft binder were found to increase with increase in binder concentration. The contact angle for the polar component was greater than the moderately polar and non-polar solvents, because of its higher water affinity compared to the moderately polar and non-polar solvents. The surface energy of the finished leather was calculated by combining both dispersive and non-dispersive components. There are several interactions taking place in the adhesion/cohesion between atoms and molecules during finishing of leathers that results in a surface energy. Dispersive interactions in leather finishing process are those caused by temporary fluctuations in the charge distribution of atoms or molecules during pigment binder interactions. Polar interactions are non-dispersive wherein Coulomb interactions between induced and permanent dipoles, such as hydrogen bonding taking place during the film formation of pigment binder interactions in finishing of leathers.[24]

The dispersive component of surface energy values for different PABR finished leathers showed a decreasing trend. However, beyond the PABR of 1:3, there was no major difference in the value of surface energy. A similar pattern was also observed in the polar component of the surface energy. Hence, it can be concluded that a ratio of 1 part of pigment requires 3 parts of very soft binder to form a film that was optimal surface energy for a better performance in finished leather. The physical properties of the finished film also followed a similar pattern as shown in Table VII. From the above observations, it can be concluded that the surface of polymer macromolecules tends to reorient or restructure in order to increase the surface concentration of both polar or non-polar moieties depending on the polarity of the surrounding phase; this phenomenon is attributed to the thermodynamic driving force to minimise the surface free energy. This indicates that a lower surface energy value in the finished film will need a less amount of energy for the finished film to be removed from the leather surface.

The higher values of adhesion work observed in Table IV indicates that higher energy is required to remove the finish from the leather. Hence, from Table IV, it can be seen that the work of adhesion value is lower for the higher PABR finished leathers indicating less energy is required to remove the finish from the leather. More so ever, the work of adhesion values is higher for polar solvents than for moderately polar and non-polar components, following a similar trend to surface energy values. The electrostatic force between the acrylic resin surface and the leather surface is important for controlling the film formation of acrylic resin towards binding of pigment in leather finishing. The cohesive force exerted by the interaction of acrylic resin molecules is greater than the solid-liquid (leather surface/water) interaction. As the binder concentration increases the lower the work of adhesion, so lesser energy is required to remove the finish from the leather surface.

Correlation between Surface Energy and Work of Adhesion Parameters for various PABR of Soft Binder

The surface energy and work of adhesion of soft acrylic binders in combination with other chemicals (pigments, fillers, wax emulsion, protein binder and water) was also carried out in line with very soft binders to understand the binding capacity of the soft acrylic binder

Table IV

Contact Angle and Surface Energy and Work of Adhesion Values for various PABR of Very Soft Binder

PABR	Contact Angle (degree)			Surface Energy (mN/m)			Work of Adhesion (mJm^{-2})		
	Water	DMSO	HD	γsv^d	γsv^p	γsv	Water	DMSO	HD
1:0.5	76.47	50.31	21.57	25.61	7.71	33.32	89.84	72.1	53.01
1:1	77.21	51.73	23.19	25.32	7.46	32.78	88.92	71.25	52.72
1:1.5	78.57	53.82	30.36	23.86	7.4	31.26	87.23	69.97	51.17
1:2	79.49	54.19	35.67	22.58	7.65	30.23	86.08	69.74	49.79
1:2.5	81.38	56.43	36.95	22.25	6.81	29.06	83.71	68.32	49.42
1:3	82.62	57.28	38.51	21.84	6.45	28.29	82.15	67.78	48.97
1:3.5	83.54	57.65	39.02	21.71	6.14	27.85	80.99	78.84	48.81
1:4	84.01	57.92	39.52	21.57	6.11	27.57	80.40	67.37	48.66

to the pigment particles. The surface contact angle for different pigment binder ratios (@1:0.5 to 1:4) (PABR) of soft binders was evaluated based on the results given in Table V. The surface contact angle increased as the soft binder concentration in the finished leathers increased. The effective binding capacity was observed at a PABR of 1:2.5, where the film starts to increase the surface hydrophobicity reducing the wettability of the leather surface. From Table V, it can also be observed that the contact angle of the polar component (water) had a greater contact angle than the moderately polar (DMSO) or non-polar solvent (Hexadecane) used for the study. This is due to high water affinity as the polar group was larger degree of contact angle. Combining the dispersive components (γsv^d) and polar component (γsv^p) of the leather surface values form the contact angle reveals the surface energy of the finished film. The dispersive component of surface energy exemplifies a constant trend upto PABR of 1:2.5 with little variation beyond this PABR. The polar component of surface energy also showed a similar pattern. The work of adhesion value is lower for the higher PABR finished leathers and do not increase drastically beyond PABR of 1:2.5. The surface energy and adhesion work of the finished leather as observed in Table V indicate that they follow a similar trend to very soft leathers with the optimal energy values reaching at PABR of 1:2.5. Similar patterns were also evident in the soft binder finished film's physical characteristics, as shown in Table V.

Table V

Contact Angle and Surface Energy and Work of Adhesion Values for various PABR of Soft Binder

PABR	Contact Angle (degree)			Surface Energy (mN/m)			Work of Adhesion (mJm^{-2})		
	Water	DMSO	HD	γsv^d	γsv^p	γsv	Water	DMSO	HD
1:0.5	79.97	46.49	34.53	22.87	9.55	32.42	85.48	74.29	50.09
1:1	80.04	52.11	34.89	22.79	7.67	30.47	85.39	71.02	50.01
1:1.5	81.13	55.39	38.25	21.91	7.27	29.18	84.03	68.99	49.04
1:2	81.59	56.54	41.04	21.16	7.43	28.59	83.45	68.26	48.19
1:2.5	83.45	57.54	49.92	18.58	8.92	27.50	81.11	67.61	45.16
1:3	84.92	58.42	50.13	18.49	8.26	26.77	79.28	67.04	45.08
1:3.5	86.04	59.72	51.74	18.03	7.97	26.00	77.83	66.18	44.48
1:4	86.63	60.05	52.01	17.94	7.71	25.65	77.08	65.96	44.38

Correlation between Surface Energy and Work of Adhesion Parameters for various PABR of Medium Soft Binder

The surface contact angle for various pigment binder ratios (1:0.5 to 1:4) of medium soft binder was also assessed. The surface contact angle increased with PABR up to 1:2 beyond which there was no major increase and hence optimized this PABR in the medium soft finished leathers. The polar group shows the higher degree of contact angle in medium soft binder finished leathers, indicating that the cohesive forces associated with water are larger than the forces involved with water-finished leather surface contact. The solid content of medium soft binder was higher when compared to soft and very soft binder. Hence, the contact angle of finished leather film was higher. The film on the leather surface had a better coverage and uniformity that resulted in larger contact angle values. As the binder concentrations increased contact angle increased up to 1:2 PABR as it makes the surface become hydrophobic in nature. The surface energy values showed a decrease with increase in PABR of medium soft binders up to PABR of 1:2. This indicates that lesser energy is required to remove the finish film from the leather surface beyond this PABR and hence we were optimized the ratio as 1:2 for medium soft binder finished leathers. The higher values of adhesion work for medium soft finished leathers observed in Table VI indicates that higher energy is required to remove the finish from the leathers up to 1:2; beyond this ratio there was not much variation of significance. Hence from Table VI, it can be concluded that work of adhesion value is required for the higher PABR of 1:2, which is the optimized ratio for medium soft binder finished leathers.

Pigment Volume Concentration (PVC) is a universal acceptance in the finishing process of leather industry worldwide. Pigment volume concentration in the finishing season is the volumetric percentage of pigment present, which is relative to the total solids present in both the pigment and the binder. Hence, the entire finishing process works on the total solids of these chemicals used for finishing of leathers.

It's perceived by many technical experts that a pigment (with varied total solids) will bind to the leathers surface with different binders (with varied total solids) at specified PB ratios as they result in identical values of the pigment volume concentration. However, this is not the case. The entire calculation of pigment-binder volume calculations is based on the total solids of the pigment and in relation to the total solids present in the binder. Ideal recipe development for finishing for enhanced physical and chemical properties of final leathers will be based on total solids and the volume concentration of pigment and binder majorly.

From the current study, it is also established that a ratio of pigment to binder 1:2 is sufficient for medium soft, 1:2.5 for soft and 1:3 for very soft binder both in terms of surface energy and work of adhesion values. It clearly establishes the fact that a pigment with a total solid of 22% required two parts of medium soft binder of 40% total solids, two and half parts of soft binder of 30% total solids and three parts of medium soft binder of 22% total solids to completely bind the pigment to the leather. There are also several other factors that influence the adherence of pigment to binder: (1) Fundamental packing characteristics of pigment; (2) type of binder employed; (3) types and amounts of special agents present; and (4) fineness of grind of the system.

The pigment volume concentration (PVC) of a finishing solution is the volumetric percentage of pigment contained in the total solids of the leather finish system that does not include any volatiles. It is the concentration at which there is enough binder present to completely

Table VI

Contact Angle and Surface Energy and Work of Adhesion Values for various PABR of Medium Soft Binder

PABR	Contact Angle (degree)			Surface Energy (mN/m)			Work of Adhesion (mJm^{-2})		
	Water	DMSO	HD	γsv^d	γsv^p	γsv	Water	DMSO	HD
1:0.5	78.13	50.01	31.75	23.54	8.28	31.82	87.78	72.28	50.83
1:1	79.13	50.54	33.45	23.13	8.12	31.25	86.53	71.96	50.39
1:1.5	81.02	51.48	35.01	22.75	7.58	30.33	84.16	71.40	49.97
1:2	82.67	53.25	36.85	22.28	6.99	29.27	82.09	70.33	49.45
1:2.5	83.48	54.05	37.23	22.18	6.62	28.80	81.07	69.83	49.34
1:3	84.31	54.93	38.12	21.95	6.53	28.28	80.01	69.28	49.08
1:3.5	85.09	55.19	38.86	21.75	6.22	27.94	79.03	69.12	48.86
1:4	86.39	55.98	39.57	21.67	5.75	27.42	77.34	68.61	48.64

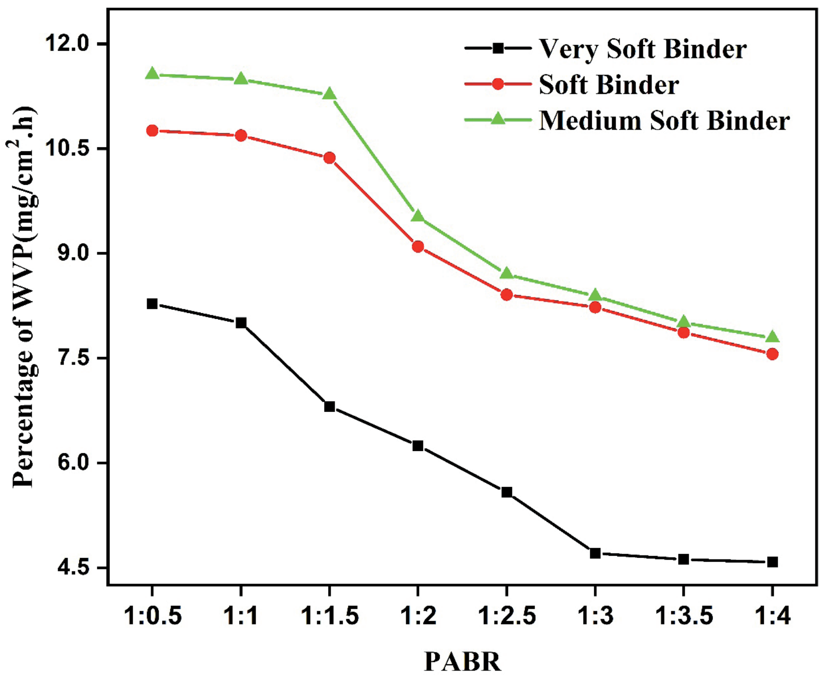

Figure 1. Plot of %WVP finished shoe upper leather versus P/B ratios.

fill the voids during the film formation on the leather surface.[25] When the pigment binder system reaches a critical pigment volume concentration (CPVC), the appearance and behaviour of the finish film on the leather surface is noticeably changed. Fundamental packing features of the pigments, the kind of binder used, types and quantities of special agents present, and the system fineness of the grind, particle size etc. all have an impact on CPVC of the leather finish system. The CPVC of individual binders used is determined by the degree of dispersion or agglomeration.[26] An agglomeration is a collection of two or more distinct pigment particles that are held together by the force of adhesion and have a tendency to stay together as one whole. A widely distributed pigment system exhibits a higher CPVC than an agglomerated pigment system. The leather finish system basically needs higher CPVC and is mainly influenced by the type of binder used. The part of the binder that was firmly adsorbed to the surface of the pigments is known as the "bound vehicle" solids. The ingredients present in the binders for leather finish systems that are also known as the "interstitial binder" are needed to fill the spaces left by the pigment particles when they are packed as tightly as possible given their dispersion. The fraction of the binder over and above the interstitial binder plus the bound vehicle solids is referred to as the "excess binder".[27] It is this excess binder that covers the pigment particle completely and does allow it to come out during wet rub fastness as soon as the film is completely formed. It is for the same reason that the finish recipe for a type of leather will have a mixture of all the three binders (soft, very soft and medium soft) with the ratios being changed to the required softness of the finish. Thus, there shall always be an "interstitial binder" and also the "excess binder" present in the finish system that protects the grain layer of the leather, binds completely to the leather as well as give the desired properties required for the type of the leather. The higher the CPVC, the smoother the surface and better the properties of the finish in the final leather; lower CPVC exhibits thixotropic effect.

Water Vapor Permeability

Water Vapor Permeability of leather determined by the rate of transmission of water vapor through leather in terms of milligrams per unit area and for a specified period. In general, unfinished leather will always show higher water vapor permeability than finished leather due to the blockage of the pores by the film.[28] Here in this work, the coating of different pigment to binder ratios on the leathers and its effect on permeability was studied and shown in Figure 1. From Figure 1, it divulges that with the increase in the concentration of binder, there is a decrease in the water vapor permeability. Amongst the binder types, the very soft binder showed less permeability than the soft and medium types. This may be due to the good covering of pores by low molecular weight components in a very soft binder. Whereas the medium and soft binders showed an almost equal range of high permeability. The presence of medium and long acrylic chains in soft and medium binders could not completely cover the nanopores present on the leather surface. Because of that medium binder will be better in order to make a permeable leather. And also, the 1:0.5 to 1:1.5 pigment to binder ratio showed higher permeability than other ratios. Hence, the water vapor permeability results confirm that the type of binder and its ratio greatly affect the permeability of leather.[29]

Finish Adhesion Properties of Finished Leather

Finish adhesion towards leather can be determined by two factors: adhesion to the substrate and cohesion within the film. Adhesion depends on the penetration of the finishing formulation either

Table VII
Adhesion Properties of Optimum PABR of various Binder

Binder Type	Finish Adhesion (N/mm)		Color Fastness to Circular Rubbing (grey scale)		Flexing Endurance (×500,000)	Lastometer	
						Distension at Grain Crack	Load at Grain Crack
	Dry	Wet	(Wet Rub)	(Dry rub)		mm	Kg
Very Soft	3.19	1.01	4/5	4/5	Excellent	8	22
Soft	2.33	0.80	4/5	4/5	Fine Grain Cracks	7	21
Medium Soft	1.32	0.71	4/5	4/5	Fine Grain Cracks	7	21

by particle size and force of action like spray or impregnation. Cohesion depends on the cohesive force within the film, which was proven to increase with decreasing particle size. Hence, it is important to understand the adhesion properties of the finished film and the grain crack resistance of the leather after coating with three types of binders. Considering the solid content of the binder, the very soft binder had a lower Total Solids content (TS -25%) and smaller particles than the soft (TS-30%) and medium soft binders (TS-36%). Higher the solid content and lower the particle size, better is the film forming characteristics and penetration of binder into the micropores of the leather. Hence, the very soft binder can coat the leather uniformly, whereas the medium type will load the leather instead of uniform coating. Similarly, the particle size of all the acrylic binders were found to be in the range of 90-140nm; lower the size of binder, the higher the impregnation/ penetration into the finish film. Similarly higher the size, more covering of the finish will be provided. From the finish adhesion property shown in Table VII divulges that due to the very small particle size, the very soft binder showed greater adhesion than medium and soft. The results are well correlated with the leather surface energy and adhesion properties.

In general, the particle size of the pigment and binder is crucial in forming the film on the leather surface. As a result, it affects the leather's surface energy and film adhesion. The good adhesion of film on the leather surface can be attained by choosing the proper pigment to binder ratio. In that way, the pigment to binder ratio was maintained at optimum ratio, the high binder concentration was chosen to get adequate binding of all pigment particles to leather, which leads to better adhesion of pigment. To understand the color transfer from leather, the wet rub and dry rub fastness was studied, and the results are shown in Table VII. At the optimized ratio of PABR, all types of binder showed good and similar fastness values indicating the better anchoring of pigment particles at higher concentrations of the binder.

To predict the film cohesion, the results of vamp flexing for leathers finished with various binders are depicted in Table VII. Throughout 10,000 cycles, all leather samples with various binders exhibit good flexing resistance, no remarkable changes were observed, and no cracks could be seen. This exemplifies the finish film's tight bond with the leather. At 500,000 cycles, the very soft binder shows no grain cracks, and the medium and soft binder showed slight creasing and cracks on the surface. The results indicate that poor cohesion in medium and soft binders caused the grain crack, whereas good cohesion in very soft binders with pigment showed good resistance against the flexing. Good flexing resistance of very soft binder is also due to the smaller particle size. Lastometer results also confirm the same observation that the distension and load were higher in the case of very soft binder than a medium and soft binder.

Organoleptic Properties Analysis

The finished leathers of all finish types were evaluated for organoleptic properties by hand and visual evaluation. The organoleptic properties such as finish film uniformity, grain smoothness, fullness, color of optimum PABR of finished leathers are given in the Table VIII. Higher numbers indicated a better property. The finish film uniformity was higher in case of very soft and soft binders, and the medium binder showed poor uniformity due to the large particle size. Grain smoothness and uniformity were interconnected based on the film coating on the surface. Both very soft and soft binder showed similar trend in grain smoothness than medium soft binder coated leather. Color shade and feel were also good for very soft binder as the grain is not loaded.

Table VIII
Organoleptic Properties of Optimum PABR of various Binder

Binder Type	Finish Film Uniformity	Grain Smoothness	Finish Surface Feel	Color Shade
Very Soft	8	8	8	9
Soft	8	8	7	8
Medium Soft	7	7	6	8

Conclusion

The study demonstrates that surface energy values play an important part in understanding surface behavior depending on the charge of the leather's surface. Because of the hydrophilic nature and particle size of the binder, the very soft binder had greater PABR than the soft and medium soft binders. The greater the surface energy values, the better the adhesive power of the binder. A better selection of binder quality and concentration is required for a better finishing procedure. It is difficult to evaluate the rub fastness test from a rheological standpoint, since the finish performance is dependent on several functions such as leather structure, application, technique, and chemical performance. The leather with higher polarity (i.e., low contact angle and higher surface energy) resulted in better work of adhesion. Hence, the present study indicates that the type of binder and PABR influence the vapor permeability of leather based on the type and solid content of binder. Adhesion and cohesion were greatly affected by the binder type; good adhesion was found in case of soft binder and good grain crack resistance in case of very soft binder. Based on the organoleptic properties, the very soft binder finished leather showed good grain characteristics than other types of binder. Thus, the study ensures that choosing correct quality and quantity of chemicals used in the finishing process, which helps us to get desired finishing. More so ever, a judicious quantity and quality of binders will be required for the type of leather based on the finish properties required.

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Super Robust, Anti-Bacterial Polyurethane Ionogel with High Sensitivity and Hydrophobicity

by

Wei Wang,[1,3] Shiyang Yan,[1,3] Yihong Zhao,[1,3] Hao Liu,[1,3] Luming Yang[1,2,3*] and Biyu Peng[1,2,3*]

[1]*National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University,* Chengdu 610065, China.

[2]*Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University,* Chengdu 610065, China.

[3]*College of Biomass Science and Engineering, Sichuan University*, Chengdu 610065, China.

Abstract

Ionogel based on ionic liquids plays a vital role in wearable electronic devices. In this study, a robust and anti-bacterial ionogel with high sensitivity and hydrophobicity is synthesized by adding 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide to thermoplastic polyurethanes at a ratio of 1:1. The ionogel not only demonstrates tensile strength of 23.1 MPa and elongation at break of 1008%, but also exhibits excellent fatigue resistance with low residual strain (8%) and small hysteresis loop. Ionic liquid makes the ionogel have high-temperature stability ($T_{5\%}$ near 300°C) and low T_g (-63.3°C). Due to the anti-bacterial property of ionic liquid, the ionogel formed by ionic liquid has anti-bacterial property, with up to 99% inhibition against *E. coli* and *S. aureus*. The sensor prepared with the ionogel shows a *Gauge Factor* of 1.8, with a short response time (128 ms) and a stable induction signal under water and at low temperature. Due to those performance characteristics, we believe that the study could provide insights for subsequent research on ionogel-based wearable electronic devices, for instance, the development of electronic skin in the leather industry.

Introduction

Nowadays, wearable electronic devices have received considerable attention due to their flexibility and stretchability, and have made significant progress in various fields, such as human movement and health monitoring,[1-3] electronic skin[4-6] and human-computer interaction interfaces.[7-9] However, the severe conditions encountered in practical applications, such as extreme temperature, dryness, humidity, and underwater environments; limit the research on flexible sensors. At present, hydrogel is most widely used in the field of wearable electronic devices because of its high conductivity, superb stretchability, and bio-tissue-like moduli.[10-14] However, due to its high-water content characteristic, hydrogel faces two challenges which must be overcome in practical applications. One is that hydrogel would freeze at low temperature, resulting in hardening. The other is that during the long-term use of hydrogel, the solvent water in hydrogel would evaporate, causing it to dry and crack. To address the two challenges mentioned above, a number of strategies have been developed, such as introducing low vapor pressure solvents glycerol[10, 15-18] and organic solvents.[19-21] However, those strategies may increase the risk of adverse reactions through skin contact.

Ionogel has a three-dimensional polymeric network structure that can be combined with ionic liquid (IL), a green and harmless solvent composed of large-sized anions and cations.[22-24] In practical use, IL has excellent electrical conductivity, low freezing point, low vapor pressure and non-toxic properties, which provide ionogel with electrical conductivity and maintains stability in extremely low-temperature environments for long-term use.[25-30] The selection of polymer materials should have good compatibility with IL and require sufficient mechanical property suitable for the intended applications. For instance, Lee et al.[31] combined poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)) with 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([BMI][TFSI]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMI][PF_6]) to prepare ionogel. Although ionogel has outstanding electrical conductivity and environmental stability, it lacks in some mechanical properties, the tensile strength of which is only about 1.8 MPa. In contrast, thermoplastic polyurethanes (TPU) are polymers with preeminent mechanical properties. According to the report, the polarity of the polyurethane (PU) chain segment makes the TPU highly compatible with ILs.[33] Therefore, it can be speculated that if the mechanical properties of TPU could combine with the electrical conductivity of ILs, ionogel can be obtained with long-lasting fatigue resistance, thus ensuring the stability of the ionogel sensor. In daily use, the ionogel sensor inevitably encounters wet environments or underwater conditions, which affects the sensing performance of most ionogels. Similarly, choosing hydrophobic IL when preparing ionogels can not only make ionogels enhance its hydrophobicity but also avoid interference from wet environments or water molecules in the process of use.[34-36]

Leather is a traditionally natural material obtained from animal skin. Although leather inherits the complex structure and flexibility of the original skin, it lacks the essential sensory ability of the skin. The layered structure of natural leather can load and carry

*Corresponding author email: pengbiyu@scu.edu.cn ; ylmll1982@126.com

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other materials. Specifically, leather can be considered a potential candidate for manufacturing high-performance electronic skin. For instance, electronic skin can be sprayed with the conductive gel described above at different monitoring points. After that, a conductive circuit can be designed by spreading the conductive silver paste to form the sensing points of various signals, such as pressure, temperature, etc. As a result, combining leather with functional materials allows leather to restore the sensing characteristics of natural skin.

In the study, we have explored a preparation process of ionogel with sensing properties. To be specific, we chose a TPU elastomer with sufficient mechanical properties and hydrophobic IL to prepare ionogel. The prepared ionogel is expected to inherit the characteristics of TPU and IL, such as mechanical properties, electrical conductivity and hydrophobicity, so as to ensure the reliability of ionogel with stable mechanical property and sufficient conductivity in practical applications. Due to ionogel's hydrophobicity, the application range of ionogel can be extended to cope with complex humid environment in practical use. In general, the study not only demonstrates ionogel's structure and mechanical properties in detail, but also discusses the anti-bacterial property and environmental stability of ionogel. After the sensor is made, the research steps into sensitivity, sensing stability, and underwater sensing performance of ionogel.

2. Experimental

2.1 Materials

ILs 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]), and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]), were purchased from Monils Chemicals (Shanghai) Co., Ltd (Shanghai, China). TPU was obtained from DuPont. Methyl ethyl ketone (MEK) was provided by Chengdu KeLong Reagents Co.

2.2. Preparation of TPU/IL ionogel

In order to select the most suitable IL to combine with TPU to obtain the ionogel with better mechanical property, TPU was mixed with different types of ILs in various solvents and eventually dried to get ionogel. After choosing the most effective IL by the above process, TPU and IL were mixed in MEK at ratios of 4:1, 2:1, and 1:1. Then, the obtained ionogel was dried out and named as TPU/IL-4:1, TPU/IL-2:1, and TPU/IL-1:1 respectively. Since the thickness of ionogel was around 100 µm, Silver (Ag) electrode could connect to both ends of ionogel to create a strain sensor.

2.3 Characterization

A Perkin-Elmer FTIR spectrometer was employed to acquire the Fourier transform infrared (FT-IR) spectra. A UV-1800 spectrophotometer (Shimadzu) was utilized to collect the UV-visible transmittance spectra. The morphology and structure of ionogel were observed using a field emission scanning electron microscope (XL-30 ESEM FEG microscope, FEI Company). A potentialstat with alternating current (AC) was used for impedance spectroscopy (Princeton, PARSTAT MC) to determine the ionic conductivity (σ_i) of the ionogel. A tensile test machine (Instron 4465) was used to analyze the mechanical properties and resilience of the ionogel with a stretching rate of 20 mm min^{-1}. A Q800 (TA Instrument) was used to carry out dynamic mechanical analysis (DMA) by testing the temperature dependence of G′ and G″ with a heating rate of 3°C/min and a frequency of 1 Hz. The digital images were captured using a Nikon D7100 camera. Hangzhou LinkZill Technology Co., Ltd. supported the wireless system. *S. aureus* ATCC 6538 and *E. coli* ATCC 25922 were incubated in nutrient broth at 37°C for 16 hours and diluted in nutrient broth to yield a density of 1×10^6 cfu/mL. Different concentration of TPU or TPU/IL-1:1 solution was incubated with the bacterial suspension for 24 hours, after which an aliquot of 200 µL of the samples was aspirated to measure OD_{600} at regular intervals. In addition, 10 µL of the bacterial suspension was spotted at intervals on nutrient agar plates along with the samples and incubated at 37°C for 24 hours for visualization of the anti-bacterial effect, which was recorded with a camera.

3. Results and Discussions

3.1 Preparation and structure of the ionogels

After combining different types of ILs with TPU, compatible raw materials with stable ionogel were selected. In subsequent studies, different proportions of TPU were mixed with IL [EMIM][TFSI] in MEK and dried to form homogeneous ionogel. The preparation process of ionogel is shown in Figure 1. The ionogel with different proportions was characterized by FT-IR, as shown in Figure

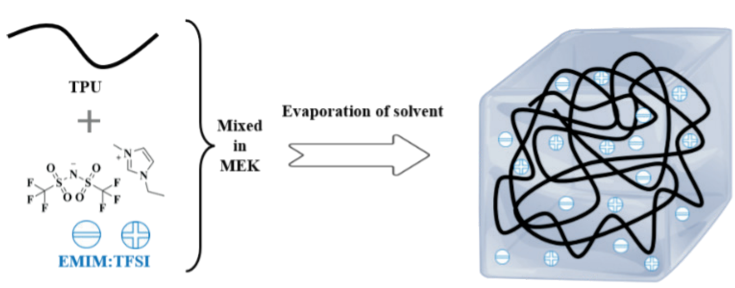

Figure 1. The preparation process of the ionogel

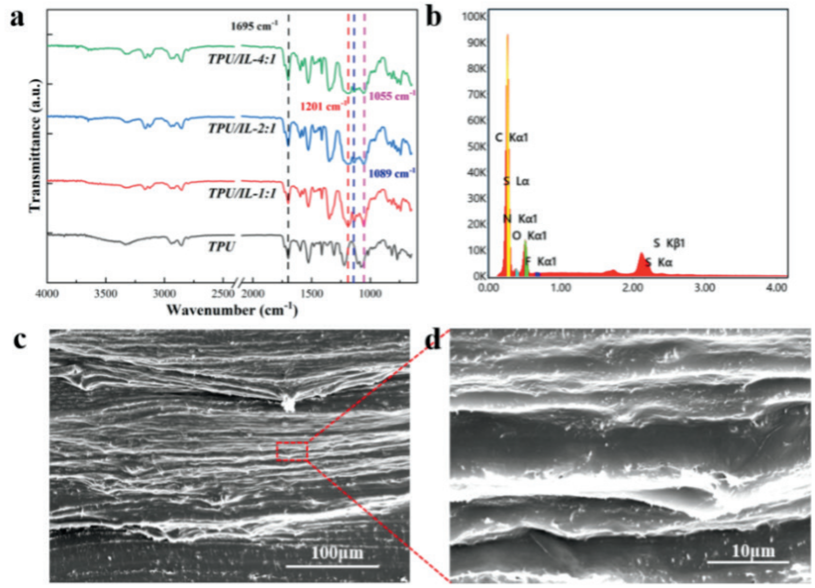

Figure 2. The characterization of TPU/IL ionogel: **(a)** FT-IR spectrum; **(b)** EDS analysis of the ionogel TPU/IL-1:1; **(c)** SEM photo of ionogel TPU/IL-1:1; **(d)** Localized enlargement of the SEM photo

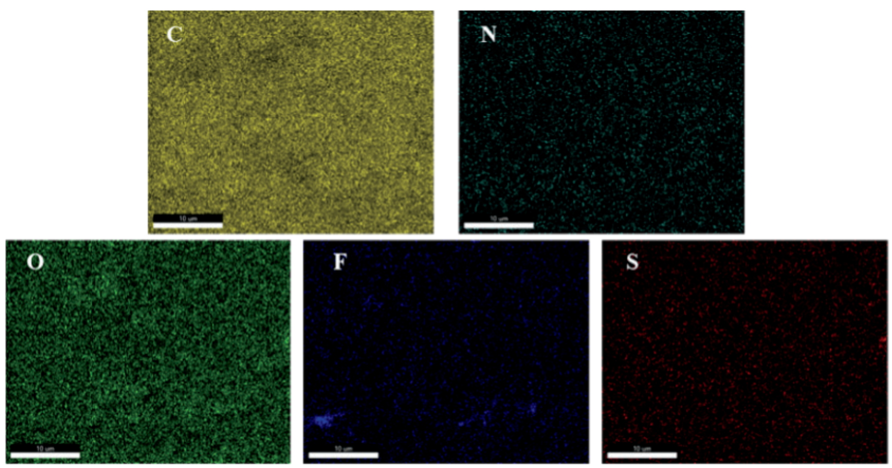

Figure 3. The EDS analysis of TPU/IL-1:1

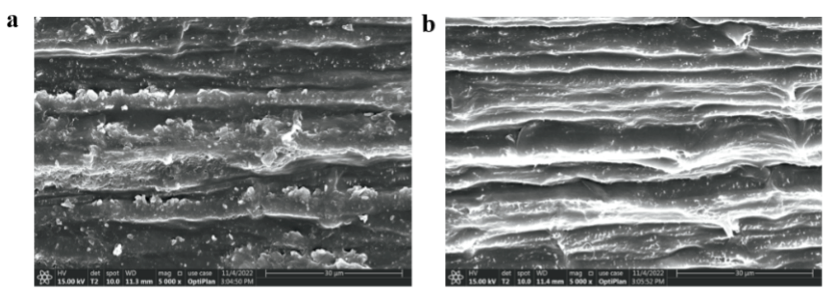

Figure 4. The SEM photo of **(a)** TPU/IL-4:1 and **(b)** TPU/IL-2:1

2a. It was obvious that the characteristic absorption peak 37 belonging to polyurethane (1695 cm^{-1}) and IL [EMIM][TFSI] (the characteristic absorption peak of S-N-S, S=O, and C-F are located at 1055 cm^{-1}, 1198 cm^{-1}, and 1201 cm^{-1}) appeared in the IR-spectra of ionogel.[37] The microstructure of the prepared ionogel was observed by SEM and EDS. The EDS analysis of TPU/IL-1:1 ionogel, shown in Figure 2b and Figure 3, demonstrated that C, N, O, S, and F elements in IL were evenly distributed in the gel system. As shown in Figures 2c, 2d, 4a, and 4b, a great number of microscopic channels can be found inside the prepared ionogel, used for conductive ion transport in IL when energized. Also, the pore size and number of the microscopic channels increase with the increasing ratio of IL. As a result, it indicates that the ionogel has been successfully prepared.

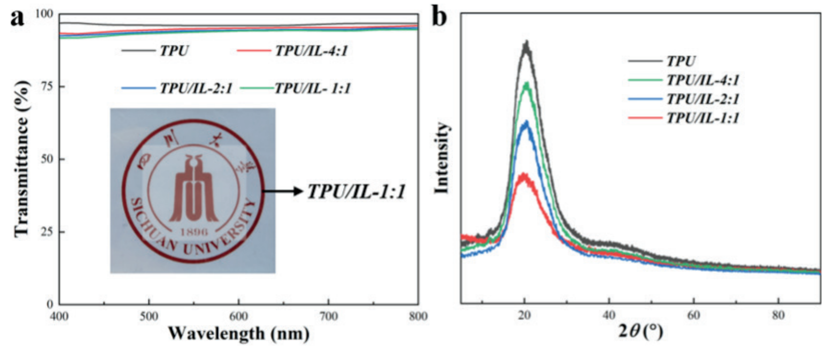

Figure 5. The structural characterization of TPU/IL ionogel: **(a)** Transmittance of ionogel (the inserted photo is the TPU/IL-1:1 on the top of the university logo); **(b)** XRD spectra

As shown in Figure 5a, all ionogel maintained a transmittance of above 90% in the visible light zone. Taking TPU/IL-1:1 as an example, it was placed on the top of the emblem of Sichuan University. The emblem could still be clearly seen through the ionosphere. The XRD results shown in Figure 5b indicated that with the increase of IL content, the crystalline part between the hard segments in the original TPU was gradually dissolved or partially dissolved. The peak intensity of the crystal was also gradually weakened at the same time. Therefore, it reflected the transmittance and crystallinity of ionogel.

3.2 Stretchability of the ionogels

As shown in Figure 6a, the mechanical property of TPU/IL-X was measured by tensile test. With the addition of IL [EMIM][TFSI] loading, the tensile strength of ionogel decreased, while the fracture strain increased at first and then decreased after adding IL. From TPU to TPU/IL-1:1, the tensile strength of the sample ranged from 55.4 MPa to 23.1 MPa, and the fracture strain varied approximately from 888% to 1037%, as shown in Figures 6b and 6c. The above mechanical behavior may be related to the swelling or dissolution ability of IL on TPU, thereby reducing micro-phase separation and crystallization of PU chains.[38, 39] To verify the mechanical durability of ionogel, each prepared material was subjected to 50% strain by continuous tensile tests, as shown in Figure 6d, Figure 7a, and Figure 7b. After ten repeated tensile tests, all samples exhibited a large hysteresis curve. Except for the residual strain of about 8% in the first cycle, the tensile strength decreased slightly in the rest of the nine tensile cycles. The hysteresis curve of ionogel was slight, with only about 4% of residual strain. The above results could be attributed to the irreversible fracture of some cross-linked points in ionogel during the first tensile process, which could not be recovered during the relaxation process. Therefore, it showed a slight decrease in strength in subsequent stretches. Since the combined effect of ionic bonds and hydrogen bonds in ionogel allowed to maintain constant tensile strength in the following nine tensile cycles, a slight hysteresis curve and reduced residual strain were observed.

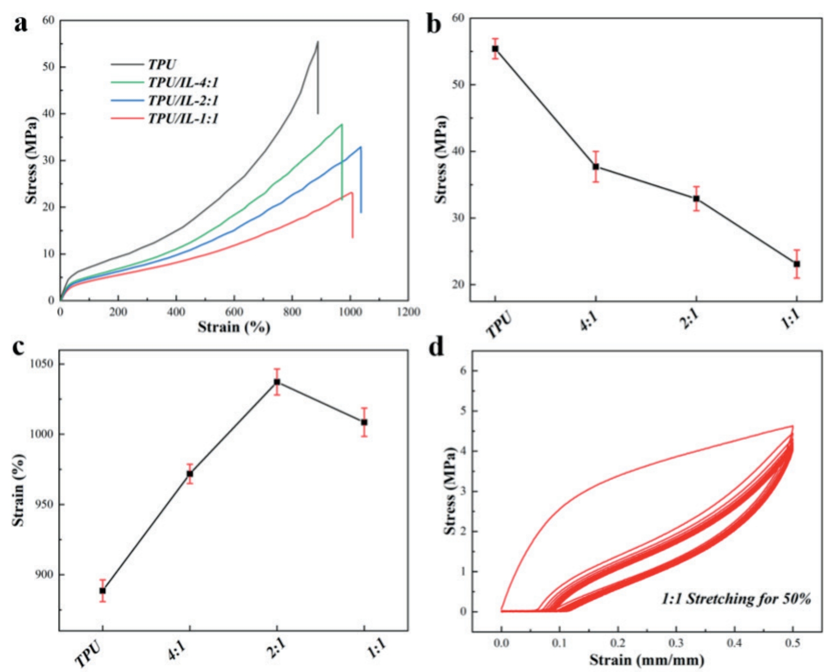

Figure 6. Stretchability of ionogel: **(a)** Stress-strain curves of ionogel with different types of ILs; **(b)** Stress data of stress-strain curves; **(c)** Strain at break data of stress-strain curves; **(d)** Different strains exerted on TPU/IL-1:1 by subsequent tensile tests

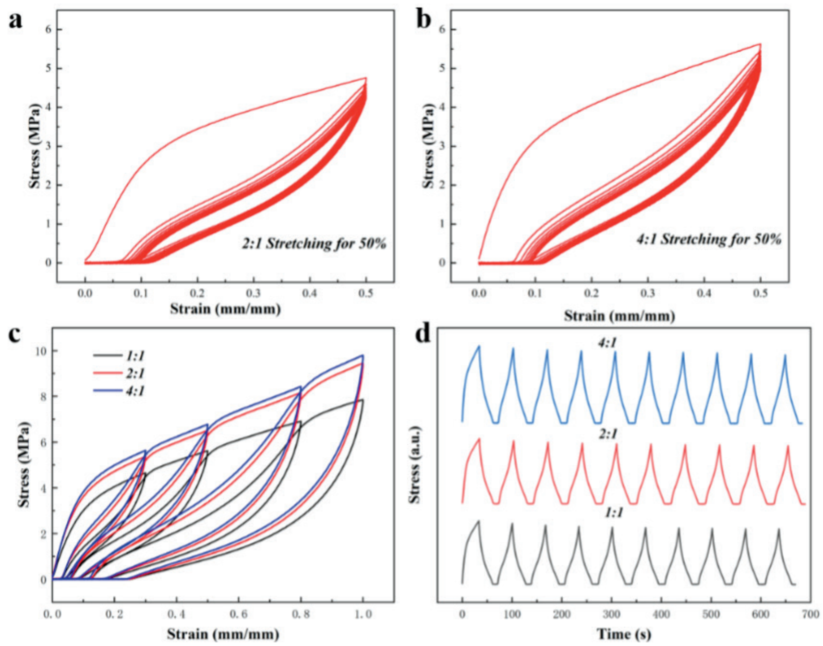

Figure 7. (a) The ten cyclic tensile tests TPU/IL-2:1; **(b)** The ten cyclic tensile tests TPU/IL-4:1; **(c)** Cyclic stretching with three ratios of different stretching rates; **(d)** Ten times tensile strength change of the same tensile rate

What is more, the tensile strength and cycle number curves, as shown in Figures 7c and 7d, indicated that all ionogel samples had stable mechanical properties, which in turn led to the expectation that, with satisfactory stretchability, the prepared ionogel could meet the functional requirements of wearable devices.

3.3 Environmental stability of the ionogels

In order to verify whether ionogel has good environmental stability, we have tested ionogel's thermal stability characterized by thermogravimetric analysis (TGA). As shown in Figure 8a, ionogel had a thermal stability of $T_{5\%}$ close to 300°C. After that, TPU/IL-1:1 was placed in an open fume hood for one month and showed little quality change during the evaluation period, as shown in Figure 8b. The above experimental results showed that the prepared ionogel had proper environmental stability and maintained a stable gel state in a heated environment or at room temperature. Moreover, as shown in Figure 8c, we have performed a dynamic mechanical analysis of ionogel to verify its transition temperature. Considering the low freezing point of ILs, ionogel presented a glass transition temperature at -63.3°C, which indicated that ionogel could remain flexible in sub-zero temperatures.

3.4 Anti-bacterial property of the ionogels

As IL has certain anti-bacterial properties,[40, 41] ionogel made of IL and TPU is expected to inherit some degree of bactericidal reactions. The experiment we did was evaluated with two common bacterial strains, including *S. aureus* and *E. coli*. As shown in Figure 9, the inhibition circle increased with the increase of IL content. To further investigate the inhibition effect of TPU/IL-1:1 against bacteria, we co-cultured ionogel with each microorganism to observe its survival rate, shown in Figures 10a and 10b. After 24 hours of co-incubation, the growth of both bacteria was inhibited,

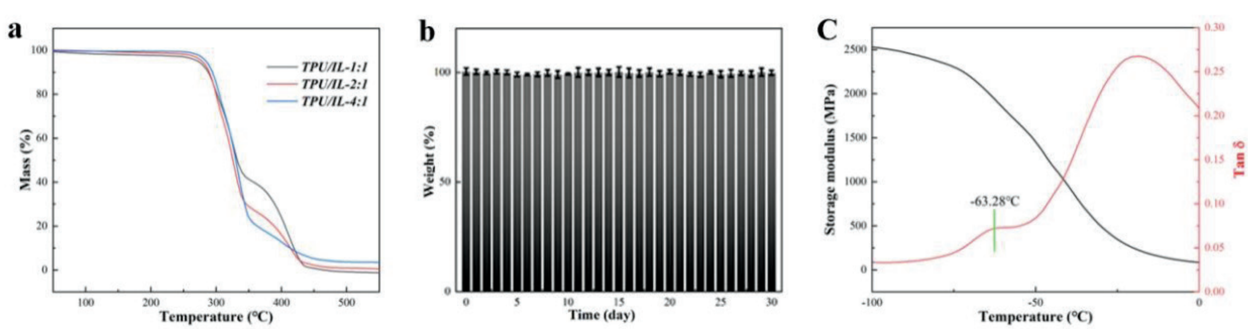

Figure 8. Environmental stability of ionogel: **(a)** TGA; **(b)** The mass changes of TPU/IL-1:1 in an open fume hood over one month; **(c)** DMA of TPU/IL-1:1

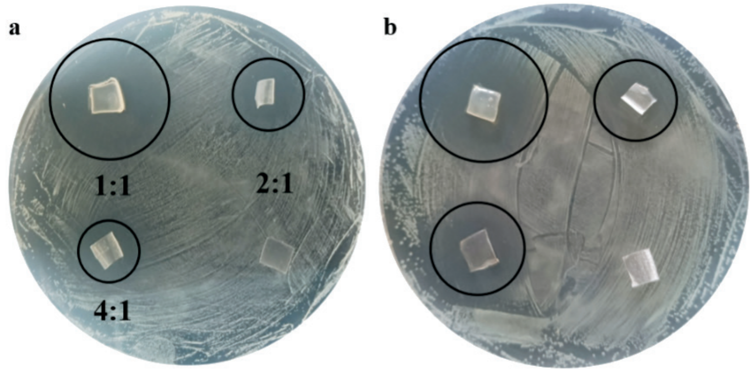

Figure 9. The inhibition circle of the ionogel with different IL contents against two bacteria: **(a)** *S. aureus*; **(b)** *E. coli*

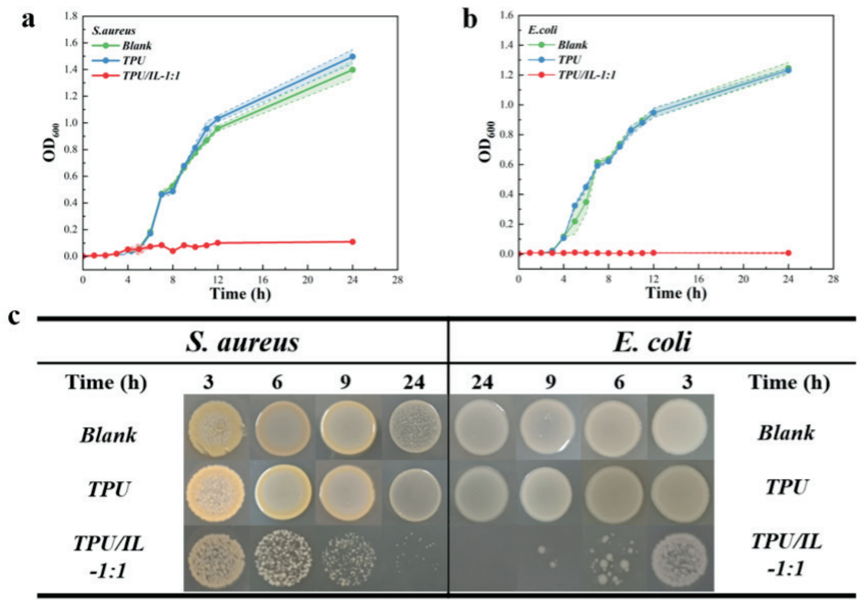

Figure 10. Anti-bacterial property of TPU/IL-1:1: **(a)** *S. aureus*; **(b)** *E. coli*; **(c)** Lithographs at different co-cultured sampling times.

and the anti-bacterial efficiency of ionogel was maintained above 99% for both microorganisms. Lithographs at different co-cultured sampling times were illustrated in Figure 10c.

3.5 The ionogels as strain sensor

As shown in Figure 11a, we measured the ionic conductivity of TPU/IL-4:1 to TPU/IL-1:1 under ambient conditions. The ionic conductivity increased with the increase of IL load from 2.1 S cm^{-1} to 11.8 S cm^{-1}, which was related to IL [EMIM][TFSI]. Also, the massive and dense channels inside ionogel facilitated ionic transportation and access to $EMIM^+$ cations.

The sensitivity of the ionogel sensor, expressed as *Gauge Factor* (*GF*), could be obtained from the mathematical fitting of the relative change of resistance ($\Delta R/R_0$) and the strain plot. The relative change of resistance varied with the mechanical strain of the sensor, as shown in Figure 11b. After fitting a straight line in the range of 0% to 150%, the slope of the curve with the variation of $\Delta R/R_0$ was 1.8 in value. Compared to other ionogel sensors reported so far,[42, 43] the prepared ionogel sensor had a relatively high sensitivity and wide sensing range. With the ionogel sensor in five cycles at different elongations with 1%, 5%, 10%, 20%, 50%, and 100%, the signal change of $\Delta R/R_0$ was shown in Figures 11c and 11d. Furthermore, five hundred cycles were performed under 50% stretch in Figure 11e. To be specific, in five hundred uninterrupted load-unloading cycles, the ionogel sensor exhibited elasticity and fatigue resistance, with little change in $\Delta R/R_0$ signal. As shown in Figure 11f, the response time of the ionogel sensor was 128ms.

Because the ionogel sensor had a low glass transition temperature, it could meet the functional requirement in the minus 20 degrees environment. Therefore, the *GF* plot could be measured in sub-zero conditions, as shown in Figure 12a. Since the sensitivity of the ionogel sensor was almost the same as the original condition, the *GF* curve could be fitted to a straight line with a slope of 1.8 even at a temperature of -20°C. As shown in Figures 12b and 12c, the

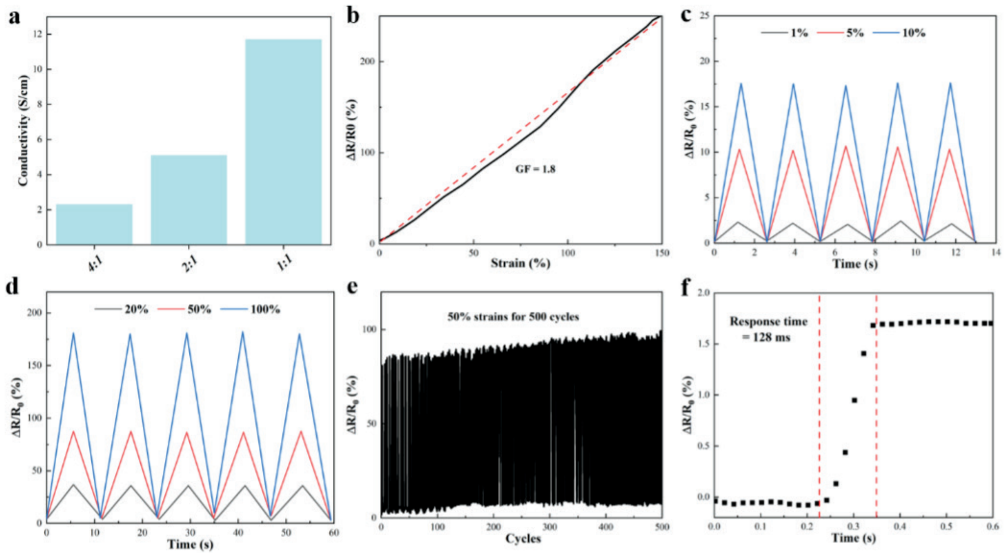

Figure 11. The strain property and relationship between stains and electrical resistance: **(a)** Ionic conductivity of ionogel; **(b)** *GF* curve of ionogel sensor; **(c)** Five successive load-unloading cycles at 1% to 10% strain of ionogel sensor; **(d)** Five successive load-unloading cycles at 20% to 100% strain of ionogel sensor; **(e)** 50% strain for 500 cycles; **(f)** Response time.

tensile test of the ionogel sensor was carried out at the same negative temperature of -20°C. The test result showed that the sensing ability ($\Delta R/R_0$ signal) of the ionogel sensor remained stable and could almost replicate the response in its original state.

Based on the hydrophobicity of IL [EMIM][TFSI], the ionogel sensor is expected to have a certain degree of hydrophobicity. In order to prove that the ionogel is hydrophobic, the sensing ability ($\Delta R/R_0$ signal) test of ionogel was conducted underwater. As shown in Figure 12d, the *GF* plot was almost the same as the original state. The variation of the sensing signal also remained stable during the cyclic stretching process, as shown in Figures 12e and 12f.

The above experiments show that the prepared ionogel sensor is not affected by either low temperature or humid environments.

3.6 The ionogel as human skin sensor

With the sensing ability for a wide range of strains and different environmental conditions, the ionogel sensor could be used to monitor various movements of the human body. In the following

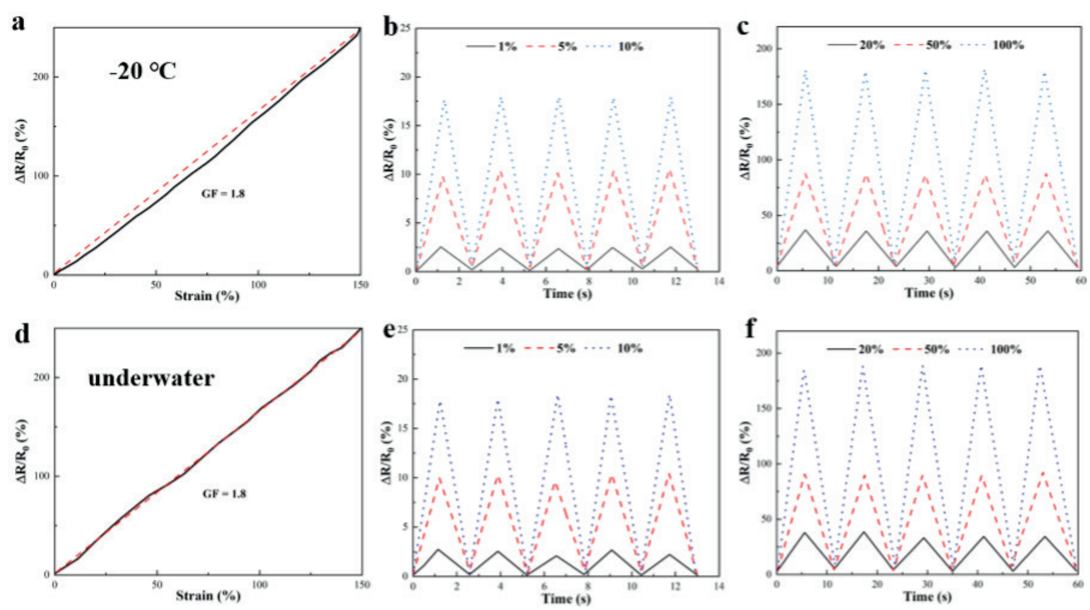

Figure 12. The strain property and relationship between stains and electrical resistance: **(a)** *GF* curve of ionogel sensor at -20°C; **(b)** Five successive load-unloading cycles at 1% to 10% strain of ionogel sensor at -20°C; **(c)** Five successive load-unloading cycles at 20% to 100% strain of ionogel sensor at -20°C; **(d)** *GF* curve of ionogel sensor underwater; **(e)** Five successive load-unloading cycles at 1% to 10% strain of ionogel sensor underwater; **(f)** Five successive load-unloading cycles at 20% to 100% strain of ionogel sensor underwater.

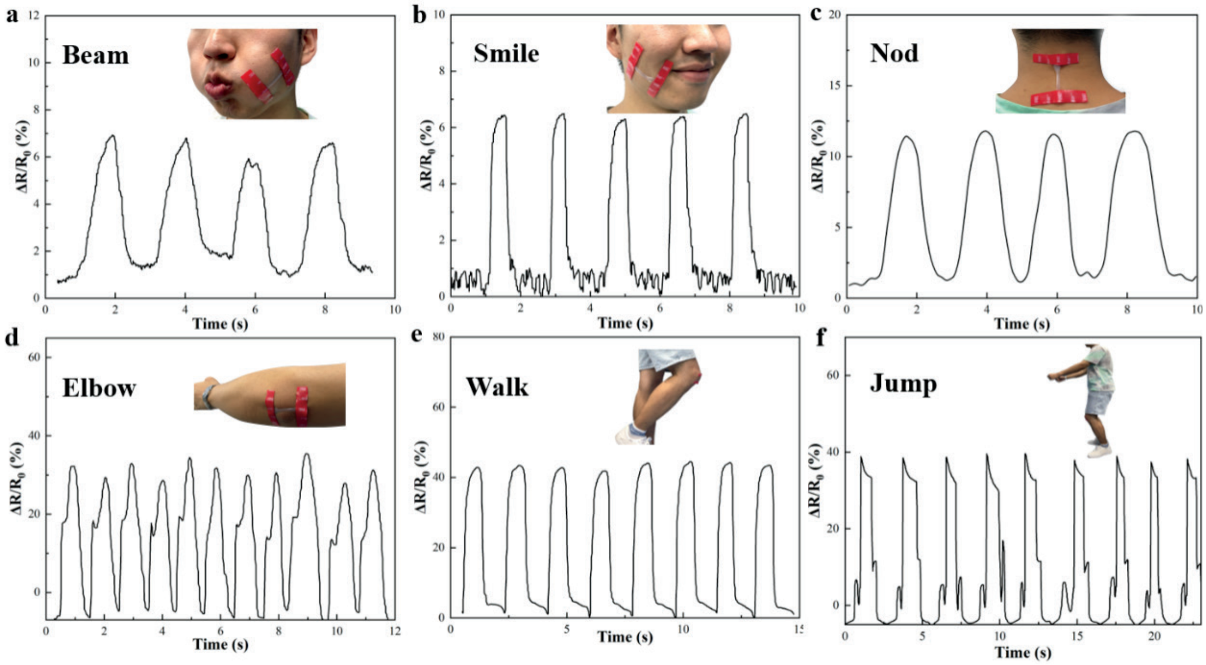

Figure 13. Relative resistance changes of TPU/IL-1:1 ionogel for various human movements. **(a)** Beam; **(b)** Smile; **(c)** Nod; **(d)** Bend elbow repeatedly; **(e)** Walk; **(f)** Jump.

experiment, the ionogel sensor was connected to a wireless system attached to different parts of the human body. Specifically, the wireless system was connected to a mobile phone via Bluetooth to monitor the real-time response of the ionogel sensor's resistance during use. The testing system could accurately detect some subtle facial expressions of the human body, such as beaming and smiling, as shown in Figures 13a and 13b. When the volunteers repeatedly performed facial expressions, the resistance of the ionogel sensor changed with the body movements, corresponding to a regular changing waveform of the mobile application interface. As shown in Figure 13c, as the volunteers bent the neck attached to the ionogel sensor, the application interface displayed the regular waveform accordingly. Unlike the results evaluated in the tensile test in the laboratory, a different waveform could be generated since the deformation of ionogel varied along with the volunteers' movements. In addition, due to the high tensile property of ionogel, large-scale movement signals of human body could even be detected, as shown in Figures 13d, 13e, and 13f. What is more, when the ionogel sensor was attached to the volunteers' elbows and knee joints, the mobile application interface showed large changes in the waveform as the volunteers walked, jumped, or repeatedly bent their elbows.

4. Conclusion

The study successfully created a robust ionogel by combining IL with TPU. The prepared ionogel not only has great mechanical property and environmental stability, but also has anti-bacterial property and electrical conductivity. By making it into a sensor, the ionogel possesses adequate sensitivity (*GF*=1.8) and a fast response time of 128ms in the strain range of 0 to 150%. Also, it has stable sensing performance even in sub-zero or underwater environments. What is more, the durability of the ionogel can be explained by the mechanical property of TPU used in its preparation process, while the ionogel's anti-bacterial property and low freezing point characteristics are inherited from the IL test. The introduction of the IL hydrophobicity further endows the ionogel with the ability to work underwater, broadening the application scenario of the ionogel sensor.

In subsequent studies, we will spray the ionogel on leather to produce electronic skin which could respond to external stimuli and make leather materials "alive." Using leather as a base material for flexible and wearable electronics demonstrates a value-added commitment to upgrade cycles for low-value leather. We strongly believe that such a design could not only lead to new flexible electronic products, but also help unlock the potential of multifunctional electronic skin. For instance, a leather insole sensor could monitor the plantar pressure distribution of the diabetic foot to help intervene and treat injuries by understanding patients' body response to the damages.

Acknowledgments

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COUNCIL CONFERENCE CALL MINUTES
AMERICAN LEATHER CHEMISTS ASSOCIATION
FALL COUNCIL MEETING
October 24, 2022

PRESENT

Officers:	Joe Hoefler, John Rodden
Council Members:	Marcelo Frago De Sousa, Roger Pinto, Myron Hooks
Executive Secretary:	Kristina Hall
2024 Convention Chair:	Donis Bosworth, Debra Crivaro

1. **WELCOME**. The meeting was called to order. It was determined that a quorum was present.

2. **MINUTES.** All previous minutes have been approved by Council.

3. **2024 UPDATE OF ANNUAL CONVENTION.** Donis Bosworth gave updates on Sponsorship campaign, and Debra Crivaro gave updates on planning of the convention.

Contract Provisions
The 2024 site will be Hershey Lodge, Hershey PA May 21 – 24, 2024. A deposit of $5,000 is on file Hershey Lodge, with additional payments of $5,000 being due 10/26/2023, $5,000 being due on 01/25/24, and final payment of $7,000 due on 04/22/2024. Deposits will cover the majority of the costs prior to the event.

The rates will be as follows:

Single	$399.60 per night, inclusive
Double	Debra will request this rate

Rates quoted are per night and include lodging, breakfast, lunch, dinner, all taxes and amenity fee. The package begins with breakfast on May 22, 2024, and ending with dinner on Thursday May 23, 2024. Deadline for reservations is Friday April 19, 2024.

The rates for pre/post arrival are as follows:
Single/Double $179.00 per room plus taxes and resort fee
Rates for early arrival include accommodation only.

Schedule
The tentative schedule will follow the same schedule as the 2023 convention.

Entertainment
Ms. Crivaro is still looking at entertainment options for Wednesday evening. She will report to the executive secretary when plans have been finalized. Suggested activities are, karaoke, ALCA talent show, or hypnotist.

Sponsorship Campaign
Ms. Bosworth requested that she be able to start the sponsorship campaign by the end of October 2023. She hopes that by approaching the sponsors prior to the end of the year they will be able to include sponsorship into their 2024 budget or have excess funds from 2023. Sponsorship levels will follow the same guidelines as 2023.

Ms. Bosworth will confer with Vice Chair Amie Kranz to get the sponsorship campaign underway. Ms. Bosworth anticipates sponsorship for much of the cost of the convention.

Sports and Social Coordinator
Mrs. Hall reported there was no need for a Social Coordinator for 2024, but a Sports Coordinator for the golf tournament will be obtained. Discussion followed about the start times for the golf tournament, Debra reported that she was able to speak directly to the Club House and they can give a start time of 11:30 a.m. and a box lunch will be provided.

Proposed Budget
A proposed budget for the 2023 convention was reviewed during the call. Motion was made to approve budget and seconded and approved. Ms. Donis anticipates coming in under budget but using sponsorship to finance the convention.

AV Person
Ms. Crivaro will find an AV Coordinator for 2024.

Technical Program – John Rodden, Chair
Mr. Rodden reports that he has been in contact with several potential presenters. Mr. Rodden discussed the participation of LHCA again in 2024 and will discuss potential presenters with Steve Sothman. There was discussion regarding making the presentations available to attendees following the convention. Mr. Hoefler reported that attendees from the 2023 convention have requested presentations. For 2024 efforts will be made to make presentations available following the convention.

Wilson Lecture – Jeff Miller, Chair
Panos Mytaros, from ECCO Leather has accepted the nomination. No further information is available at this time.

Alsop Award – Joseph Hoefler, Chair
It was decided that since the approved recipient of the ALSOP Award for 2023 was unable to attend the convention, they would be asked to attend the 2024 convention to receive the award.

O'Flaherty Service Award – Sarah Drayna, Chair
A follow up with Sarah Drayna via email following the meeting confirmed that nominee Andreas Rhein was submitted and approved as recipient at the 2024 convention.

2025 Convention Site
This item was tabled until further discussion with LHCA, on the dynamics of a joint convention are discussed.

4. **FINANCIAL REPORTS** – Kristina Hall

Year to Date Financial Reports
Council reviewed the Profit and Loss Statement and Balance Sheet through October 23, 2023. It was noted that financials and bank accounts have been moved from Wells Fargo Bank to PNC Bank. Due to changes in the investment accounts the balance on the report was not accurate. Further discussion is needed with Mr. Lehman on posting these changes.

The Membership Breakdown as well as a dues and subscriptions breakdown for 2024 was emailed to Council prior to the meeting and reflected the following:

118 Active, 45 Active Life, 4 Active Life Mutual, 22 Active Life Retired, 15 Active Mutual, 39 Active Retired, 2 Students, and 27 SLTC along with 3 SLTC Students, for a total of 275 members. Out of the above membership that is anticipated for 2024, dues will be collected from 132 paying members, excluding the dues that will be collected from the SLTC members. The list of canceled memberships was reviewed. There are 45 subscriptions that have been invoiced for renewal for 2024.

Ms. Hall also noted that 1 advertisers have committed for 2024. The other five 2023 advertisers are still awaiting approval from their company.

Motion was made, seconded and passed to accept the Financial Reports as submitted.

A rough draft of the 2024 Association Budget was sent to the Council prior to the meeting. Motion was not made for approval will table until January meeting.

5. **EDITOR'S WRITTEN REPORT** – Steve Lange
The Editor submitted the following report which was emailed to Council.

Editors Report: October 22, 2023

On track to publish 46 papers for 2023.

2022 Convention & 2023 Convention information were both published in 2023.

The flow of papers has slowed. We normally have about 5 months of papers in the pipeline. We are down to about 2.5 to 3 months in advance. I only have four papers with reviewers and one paper pending final revision. Below is a summary of submissions over the past few years:

	2020	2021	2022	2023
January	6	5	5	2
February	5	5	8	9
March	3	3	5	8
April	3	4	3	6
May	5	4	2	3
June	5	4	5	6
July	7	6	7	3
August	4	11	5	4
September	4	4	5	2
October	4	9	3	2
November	3	8	2	
December	9	8	3	
	58	71	53	45

I can reduce the number of papers per issue (which will reduce our costs) if the shortage continues.

Still working with UC Press to get old issues published online.

Submitted by:
Steve Lange
JALCA Editor

6. **WAYS AND MEANS COMMITTEE REPORT** – Leroy Lehman
Mr. Lehman was not present at the meeting, so no report was given. Ms. Hall did report that per the September statement the Home Depot stock has been sold and J.P. Morgan has been purchased.

7. **TECHNICAL COMMITTEE REPORT**
Ms. Hall reported that the Correspondence Course has one student who has completed the course and is awaiting grading and there is one new student, who joined ALCA in 2023.

8. **NOMINATING COMMITTEE REPORT** – John Rodden Chair
No names were submitted at this meeting. Mr. Rodden stated that he had 2 candidates for council in mind and will discuss further with Mr. Hoefler for additional candidates and a candidate for the Vice President position becoming vacant.

9. **OLD BUSINESS**
This item was tabled until January.

10. **NEW BUSINESS**
Ms. Hall reported on her attendance at the LHCA meeting. The LHCA meeting attendance does offer the potential of approximately 25 participants to convention that are not members of ALCA. Inquiries were made by attendees into the correspondence course that the ALCA offers. Contact information on possible sponsors from LHCA will be forwarded to Ms. Bosworth. Discussion for reimbursement of expenses is to be shared with LRL. Further discussion will be had amongst Mr. Hoefler, Mr. Rodden, and Mr. Lange of LRL.

11. **LOCATION AND DATE OF NEXT COUNCIL MEETING**
Next Council conference call will be in January. A date will be circulated closer to that date.

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

Respectfully submitted,

Kristina Hall, Executive Secretary


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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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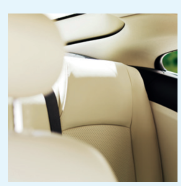

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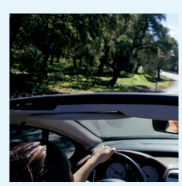

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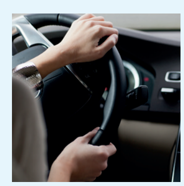

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Journal Publication Policy

1 – SUBMISSION
Manuscripts, which meet the following requirements, should be submitted in electronic format to: jalcaeditor@gmail.com as a single Word e-mail attachment (including embedded Figures and Tables in JPG and/or Excel).

2 – SUBJECT MATTER
The *Journal of the American Leather Chemists Association* publishes manuscripts on all aspects of leather science, engineering, technology, and economics, and will consider related subjects that address concerns of the industry. Examples: hide/skin quality or utilization, leather production methods/equipment, tanning materials/leather chemicals, new and improved leathers, collagen studies, leather by-products, impacts of changes in leather products industries, process efficiency, sustainability, regulatory, safety, environmental, tannery waste management and industry economics.

3 – TYPES OF ARTICLES
Four categories articles are considered: **Technical Papers, Technical Notes, Reviews and Invited Lectures.**

Our major publication emphasis, **Technical Papers**, should be a thorough treatment of a specific subject, including such figures and tables (F&T) necessary to illustrate the points made in the text and to justify the conclusions drawn. Technical Papers are subject to peer review prior to acceptance.

Technical Notes accommodate less formal presentations from the tanning industry and suppliers, especially those made at the Association's annual meetings. Notes from the supplier industries should include technical data to justify the statements made. Notes, while less formal, must meet the literary standards of the *Journal*, but need not contain an experimental section or references and are usually not Peer Reviewed.

Review Papers and **Invited Lectures** will be published only on currently important theoretical or practical aspects of leather science, manufacture, and economics and must meet *Journal* literary standards.

4 – GENERAL REQUIREMENTS FOR MANUSCRIPTS
English Language: Manuscripts must be submitted in native American English language consistent with *Journal* standards and sufficient to enable Peer Review of technical content.

The **first page** should have a running head, title, authors' last names with initials, (corresponding author footnoted with e-mail address) and authors' affiliations/addresses. Also footnote occasion, place and date of presentation on which the paper is based if appropriate.

While some formatting flexibility is permitted, it is recommended that **Technical Papers** be submitted with the following sections:

- **Abstract** Tells why the work was done and may generally state results (minimize data details) and their significance in one paragraph.
- **Introduction** Must judiciously reference using superscripts (ex…word.[6,7]) the important contributions to the subject that have been previously published, clearly state how the work in the submitted manuscript differs from the cited work and satisfy reviewers' determination of originality.
- **Experimental** Must be detailed enough to permit other investigators to verify the work, including the source and grade of all chemicals used and detailed descriptions of processes and equipment used to conduct the experiments.
- **Results** The actual data obtained should be given under Results. The interpretation of this data should be under Discussion.
- **Discussion**
(Results and Discussion may be combined if clarity can be retained).
- **Conclusions** Brief and based on the reported results.
- **Acknowledgement** Necessary credits appear here.
- **References** Required for all citations (matching sequential numbering as used above, but generally limited to no more than about 20 but additional references will be acceptable if critical to the work) adhering to *JALCA* format; Examples:

1. Liu, C. P., White, R and McClendon, M. D.; Energy Approach to the Characterization of the Thermal Resistance of Leather. *JALCA* **92**(4), 103-118, 2007. [*JALCA* **92**, 103-118, 2007 also acceptable]
2. Trade Practices for Proper Packer Cattlehide Delivery, 3rd ed., Leather Industries of America and U.S. Hide, Skin & Leather Association, pp. 12-19, 1993.

This *Journal* is referenced as *JALCA*: for other journals, use the Chemical Abstracts abbreviations. Use of "In press" and web addresses should be limited.

5 – FURTHER REQUIREMENTS FOR MANUSCRIPTS

Length should generally not exceed 16 single spaced (24 double-spaced) pages of typed text, including embedded Figures &Tables; using 12 point Times New Roman font with paragraphs not indented. The manuscript should contain reproduction quality figures and tables embedded at the appropriate locations in the text, thus offering the entirety of the manuscript as a single Word document.

Figures and Tables (F & T)

Figures (numbered with Arabic numerals) are preferred with images submitted in JPG format as black and white or color. The electronic *JALCA* issue will reproduce color as submitted. Excel table data should preferable be converted to and presented in JPG image format whenever possible.

Tables (numbered with Roman numerals) presented in Excel format should be used only when there is no other way to reasonable present accurate readable data. Excel formatted tables must have a width of no greater than 3.5 inches (9 cm.) or 7.5 inches (19 cm.) and embedded in the Word text in a way that most closely follows the flow of the manuscript. F&T should be numbered consecutively with designated numerals.

To aid the reader, the total number of compliant F&T is recommended to be no more than eight (8) per manuscript unless having additional F&T will help present complex data in a logical fashion. If too many F & T are used, the author(s) will be so advised during the review process.

For a comprehensive overview of all manuscript requirements authors are urged to review manuscripts in recent copies of the *Journal*.

6 – "LIFE LINES"

Every manuscript should be accompanied by a brief biography of each of the authors or the citation of an earlier "Life Line" biography.

7 – PUBLICATION RIGHTS

Authors of papers to be published in the *Journal* will be required to sign a "Transfer of Copyright" form before the paper is published. All papers based on oral presentations at the annual meetings of the ALCA are the property of the Association with the Journal having the exclusive right to publish. Authors employed by a U.S. government agency will be required to provide an employee certification.

Contents of papers published in the *Journal* may not be republished elsewhere without the written permission of the Journal Editor. Permission will be granted for publication of the entire paper in non-English-language publications or for summaries of the paper along with reference to the complete article in *JALCA* in English-language journals.

8 – PEER REVIEW

Two members of the Editorial Board will review editor pre-screened manuscripts. The reviewers' evaluate:

1. Interest to Subscribers (compliance with Subject Matter policy),

2. Originality (Introduction must make this case),

3. Scientific/technical validity (experimental design, results justify conclusions, controls, statistical validity with appropriate use of standard deviations),

4. Literary standards (English language readability, grammar, subject tense/verb matches, etc.),

Reporting the results to the editor on ReviewformXX.

The reviewers' written recommendations will be e-mailed to the corresponding author; who then must respond to all of the reviewers' recommendations with a revised manuscript (response may include separately explanations of specific disagreements with the recommendations). Other than inappropriate subject or lack of originality, most papers can be rendered acceptable for publication by this revision process.

The *Journal* Editor makes the final decisions as to acceptability and scheduling of manuscripts for publication in *JALCA*.

9 – PROOFS AND REPRINTS

When formatted, the editor will e-mail a PDF galley proof to the corresponding author. The author will have 3 - 4 days to respond to the editor with suggested final changes. Final changes are restricted to editorial type changes. Technical changes will not be allowed and, if requested, may result in the manuscript being dropped from the planned issue.

10 – CONFLICT OF INTEREST POLICY

All authors are expected to identify and disclose any potential conflicts of interest that may impact their work. A statement regarding any or no Conflicts of Interest must be included in all manuscripts.

Reprints of *Journal* articles may be requested through the ALCA website: **leatherchemists.org** or by emailing: **hallks@ucmail.uc.edu**

The American Leather Chemists Association

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The ALCA office is working to compile a complete collection of issue of *The Journal of the American Chemists Association.* If you or someone you know has copies of these missing issues you would like to donate to ALCA please contact the ALCA office.

Missing issues needed.

1924 - January

1937 - January and December

1939 - January, March and April

1940 - January

1946 - February

Lifelines

Roza Mirzamuratova graduated from the Faculty of Light Industry in 1998 in the city of Taraz and worked as a design engineer at the factory, after which she taught at college. Since 2011, she has been teaching at the M.Auezov South Kazakhstan University. In 2020 she became a doctoral student of M. Auezov South Kazakhstan University Textile and Food Engineering High School, Technology and Design of Light Industry Products Department, Shymkent, Kazakhstan conducting research on the leather industry, has completed an internship at the Ege University. Completed internships in Italy, Turkey and Romania in the framework of ERASMUS +REILEAP –Reinforcing capacities of HEIs for leather and leather products in Uzbekistan-Kazakhstan.

Eser eke bayramoğlu is the world's first female leather professor in the field of leather. She is working as full Professor at Ege University, Faculty of Engineering, Department of Leather Engineering. Currently teaching Leather Microbiology, Hazardous Fungi During Leather Production, Leather Production Practice, Microorganism Control for the Leather Industry, Finishing materials and techniques, Leather handicrafts, Marketing, Parchment Production Technology. She has relevant skills and rich experience on the research of leather making technology and new product development from green chemicals. She also gives lectures about leather technology abroad. Twenty-four awards have been won since 1993 including 17 publication awards. She created a microbiology laboratory in her department. She also worked, as an official consultant, with her graduate students in the establishment of a cosmetic company, Flamel Chemistry, which produces keratin from waste hair and wool.

Rashid Kaldybayev assistant professor at M. Auezov South Kazakhstan University, Textile and Food Engineering High School, Technology and Design of Light Industry Products Department, Shymkent, Kazakhstan. Currently teaches Technology of Light Industry Products, Materials Science, Confection of Materials. Six research projects were carried out, including 2 projects in the framework of ERASMUS. Forty-six articles were published in the Scopus database. A lot of research has been done in the field of Textile and Light Industry.

James Kihara obtained a Bachelor of Science degree in Leather Technology from Dedan Kimathi University of Technology, graduating in 2019. Presently, he is concurrently pursuing a Master of Science in Leather Technology at the same institution while holding the position of Graduate Assistant. His research pursuits are centered around the realm of eco-friendly tanning methods, reflecting a commitment to sustainable practices within the leather industry. Accumulating a total of two years in the domains of teaching and research, Mr. Kihara's endeavors exhibit a dedication to the advancement of knowledge and expertise in his chosen field. His work includes a peer-reviewed publication on the extraction and characterization of tannins from banana midribs. Through his scholarly contributions, Mr. James Kihara underscores his enthusiasm for exploring innovative and environmentally conscious approaches within the realm of leather technology.

Benson Ongarora is an accomplished chemistry lecturer with over twelve years of experience in teaching and research in the Department of Chemistry at Dedan Kimathi University of Technology. Benson holds a doctorate degree from Louisiana State University, having completed his studies in chemistry in 2012. His specialty in organic chemistry serves as a good foundation in material chemistry and his skills in synthesis, isolation, characterization and analysis, which have catapulted him to carryout research in various fields. He has successfully supervised six students at Master's level both in the area of chemistry and leather technology. His research in leather technology includes tannage of chamois using oil extracted from tannery fleshing waste among other materials. He has more than eighteen publications in peer reviewed journals on various subjects. He is a reviewer with Team Publons, a part of Web of Science group, besides reviewing for *Journal of the American Leather Chemists Association* (*JALCA*).

Douglas Onyancha earned a Bachelor of Science degree from Egerton University in 2002, followed by the completion of a Master of Science in Chemistry from the same institution in 2006. Subsequently, he pursued a PhD in Chemistry at Nelson Mandela Metropolitan University, successfully graduating in 2010. With a research emphasis on organometallic compounds and their versatile applications across industries such as leather production, drug delivery, and catalysis, Dr. Onyancha has accrued over 13 years of valuable research experience. As an accomplished academic, Dr. Onyancha has taken on the role of a lecturer within the Department of Chemistry at Dedan Kimathi University since 2012. His dedication to advancing knowledge in his field is evidenced by his publication record, which boasts more than 15 peer-reviewed articles. Organometallics and their dynamic role in material development constitute the primary focus of his scholarly work. Furthermore, his research extends to the realm of cleaner production technologies, where he strives to engineer eco-friendly alternatives to hazardous chemicals in the realm of materials synthesis. In the landscape of academia and research, Dr. Douglas Onyancha's contributions stand as a testament to his commitment to innovation and sustainability within the realm of chemistry and materials science.

M. Suriya is currently working as a Project Assistant in CSIR-CLRI. He has completed his M.Sc. degree in Biophysics and has expertise in biophysical chemistry, and surface sciences. His primary research focus in CSIR-CLRI has been on surface properties of finished leathers, where he has effectively utilized his technical expertise for the benefit of the leather sector.

Mishamo Wakaso is currently working as CEO, Leather Technology Sector in Leather and leather products research and development centre (LLPI-RDC) where he oversees and leads important initiatives aimed to advancing the leather industry in Ethiopia. His expertise as production chemist, quality control chemist and wet end process quality control chemist, utilizing his technical expertise has significant contributions to the leather processing industry in Ethiopia.

Sathya Ramalingam received her B.Tech, M.Tech, and Ph.D in Leather Technology from Anna University, Chennai. She is currently working as a Scientist in the Leather Process Technology Department at CSIR-Central

Leather Research Institute. She has made significant contributions to the design and development of innovative chemicals for sustainable leather processing.

Swarna V Kanth is a Chief Scientist at the Centre for Human and Organizational Resources Development (CHORD) at CSIR-Central Leather Research Institute (CSIR-CLRI), Chennai. She has been contributing to the field of leather science and technology for the past 28 years and specializes in leather biotechnology, enzyme technologies applicable for environmental applications and cleaner leather production. She has 70 international research publications, 150 Indian and international conference research papers and a patent to her credit. She has notable achievements in human resource development in providing technically trained human resources to the Indian leather and leather products sector at various levels of management. She has a strong expertise in the creation of an international skill ecosystem for the leather sector of the respective countries which has benefitted participants from over 30 countries.

Wei Wang received his Master's Degree (2012) in Fashion Design and Engineering from Sichuan University, China. Then he works in the Department of Fashion Design at Sichuan University. He was a visiting scholar at Birmingham City University, UK, from 2015 to 2016. Now He is a Ph.D. candidate in the National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University, China. Recently, his research work mainly focuses on leather products engineering and materials.

Shiyang Yan is a postdoctoral researcher at Intelligent Clothing and Sports Biomechanics Laboratory, Sichuan University, China, working on garment ergonomics and footwear biomechanics. Her main research interests include human movement simulation, finite element analysis of clothing, and providing podiatrists with orthopedic footwear design solutions. She has published over 20 papers in domestic and foreign academic journals as the first author or correspondent author and obtained 3 authorized invention patents and 1 software copyright.

Yihong Zhao received her Master's Degree (2021) in Leather Products Engineering and Materials from Sichuan University, China. Now she is a Ph.D. candidate at Intelligent Garment and Sports Biomechanics Laboratory, Sichuan University. Her main research interests include functional footwear and leather products, human movement simulation, finite element analysis of garment.

Hao Liu received his Bachelor's Degree (2021) in Light and Chemical Engineering from Sichuan University, China. Now he studies for his Master's degree in the Department of Fashion Design, Sichuan University, China. Recently, his research work mainly focused on leather product engineering and materials.

Luming Yang received her Master's Degree (2004) in Leather Chemistry and Engineering from Sichuan University, China, and the Ph.D. (2007) in Chemistry and materials technology from Tomas Bata University in Zlin, Czech. Now she is a Professor in Department of Fashion Design, Sichuan University, China. Her broad research fields are functional and intelligent clothing design, footwear and health, foot biomechanics, with a particular focus on functional garment and sports biomechanics.

Biyu Peng received his Master's Degree (1994) and Ph.D. (1999) in Leather Chemistry and Engineering from Sichuan University, China. He pursued his postdoctoral research work as a visiting scientist in Leather Research Institute of Texas Tech University, USA, from 2004 to 2006. Now he is a Professor in National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, China. Recently, his research work mainly focuses on waste resource utilization and biochemistry technologies in leather manufacturing.

INDEX TO ADVERTISERS

CALL FOR PAPERS

FOR THE 118th ANNUAL CONVENTION OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Hershey Lodge, Hershey Pennsylvania
May 21–24, 2024

If you have recently completed or will shortly be completing research studies relevant to hide preservation, hide and leather defects, leather manufacturing technology, new product development, tannery equipment development, leather properties and specifications, tannery environmental management, or other related subjects, you are encouraged to present the results of this research at the next annual convention of the Association to be held at the Hershey Lodge, Hershey Pennsylvania, May 21–24, 2024

Abstracts are due by March 1, 2024
Full Presentations are due by May 1, 2024

They are to be submitted by e-mail to the
ALCA Vice-President and Chair of the Technical Program:

John Rodden
Union Specialties, Inc.
3 Malcom Hoyt Dr.
Newburyport, MA 01950
E-mail: johnrodden@unionspecialtiesinc.com

The **Abstract** should begin with the title in capital letters, followed by the authors' names. An asterisk should denote the name of the speaker, and contact information should be provided that includes an e-mail address. The abstract should be no longer than 300 English words, and in the Microsoft Word format.

Full Presentations at the convention will be limited to 25 minutes. In accordance with the Association Bylaws, all presentations are considered for publication by *The Journal of the American Leather Chemists Association*. They are not to be published elsewhere, other than in abstract form, without permission of the *Journal* Editor. For further paper preparation guidelines please refer to the *JALCA* Publication Policy on our website: leatherchemists.org

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Steven D. Lange, *Journal* Editor
The American Leather Chemists Association
E-mail: jalcaeditor@gmail.com
Mobile Phone (814) 414-5689

118th ALCA ANNUAL CONVENTION May 21 – 24, 2024 Hershey Lodge, Hershey PA

Featuring the 63nd John Arthur Wilson Memorial Lecture

***By* Panos Mytaros**
Chief Executive Officer
ECCO

Tentative Schedule

Tuesday, May 21

Golf Tournament, Opening Reception and Dinner

Wednesday, May 22

John Arthur Wilson Memorial Lecture All Day
Technical Sessions, Fun Run, Reception and Dinner

Thursday, May 23

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

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


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