Effect of Different Retanning Systems on Surface Properties of Leather

by

S.V. Kanth, A. Ipe, B. Madhan, R. Venba and A. Dhathathreyan*

Central Leather Research Institute
Adyar, Chennai-600020, India

Abstract

The present work attempts to analyze the surface properties of crust leathers processed using different syntans of the type phenol-naphthalene formaldehyde condensate, phenol formaldehyde, melamine formaldehyde, gluteraldehyde, styrene maleic anhydride, acrylic polymer, sulphone and heterocyclic N-methylol. Contact angles of liquid drops on the leather surfaces have been used to evaluate surface energy, acidity, basicity, polarity, work of adhesion and surface roughness. The surface energy component showed that the control crust leather without retanning is practically monopolar basic with γ_{S^-} = 13.02 mN/m. Acrylic polymer retanned crust leather exhibited high basic character (γ_{S^-} = 33.15 mN/m), while phenol formaldehyde retanned crust leather had the least values (γ_{S^-} = 1.03 mN/m). The surface behavior towards rub fastness and adhesion of finish has been significantly altered by the retanning systems in leathers and showed a good correlation with the surface properties like surface charge, polarity, roughness and work of adhesion.

Abstracto

El presente trabajo procura analizar las propiedades superficiales de los cueros semi-terminados procesados usando diversos sintanes del tipo condensado del fenol-naftalina formaldehído, fenol formaldehído, melamina formaldehído, glutaraldehido, anhídrido estireno-maleico, polímero acrílico, sulfónico y de N-Metilol heterocíclico. Los ángulos del contacto de gotas líquidas en la superficie del cuero se han utilizado para evaluar la energía superficial, la acidez, la basicidad, la polaridad, la adherencia y la aspereza de la superficie. El componente de energía de la superficie demostró que el cuero semi-terminado de control sin recurtido es prácticamente monopolar básico con γ_{S^-} = 13.02 mN/m. El cuero semi-terminado recurtido con polímeros acrílicos exhibió un carácter altamente básico (γ_{S^-} = 33.15 mN/m), mientras que el cuero semi-terminado recurtido con formaldehído fenólico tuvo los menores valores (γ_{S^-} =1.03 mN/m). El comportamiento superficial en cuanto a las solideces al frote y la adherencia del acabado ha sido alterado perceptiblemente por los sistemas recurtido en los cueros y demostró una buena correlación con las propiedades de la superficie como la carga superficial, la polaridad, la aspereza y la adherencia.

Introduction

Leather, being natural material has amphoteric behavior. The surface charge of the leather is a measure of its polar nature and capacity to react with polar substances. Generally surface charge densities depend decisively on the kind of tannage and are of particular importance for all post-tannage processes such as neutralization, retanning, wetting, dyeing and fatliquoring. The post tanning processes always involve treatments with compounds in their ionized form, i.e. in the form of charged particles, which react first on the surface, so that the surface charge gets modified, affecting in turn subsequent treatments. Hence the process is to be carried out in such a way that the surface charges of crusts facilities anchorage of the finishing chemicals.

Surface free energies have been correlated with many important properties of textiles[1-3]. The total surface free energy of solid at equilibrium with vapor phase (indicated by γ_{SV}) can be estimated from the Young's equation[6].

$$\gamma_{SV} = \gamma_{LV} \cos\theta + \gamma_{SL} \quad (1)$$

(γ_{SV} is also denoted as γ_S). The Young's equation[6] is also used to measure the individual γ_{SL} (where S is the solid phase or here leather and L is the liquid) as shown in scheme 1.

Scheme 1: A liquid drop at equilibrium at the three phase contact line (SV, SL and LV)

Here θ is the contact angle made by any liquid in contact with the leather surface at the beginning of any operation. γ_{SV} is the solid surface energy and γ_{SL} is the interfacial energy between S and L.

* Corresponding Author - E-mail: chordchem@yahoo.co.in
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TABLE I
Experimental Post Tanning Process

MATERIAL: Goat skins, Wet blue, Indian, shaved to 0.9 -1.0 mm				
WASHING	200 %	Water, 35°C	20 min	pH 3.2
	0.2 %	Acetic acid, 85%		
RECHROMING/	150 %	Water		
NEUTRALISATION	4 %	Chrome syntan	60 min	
	1 %	Neutralizing syntan		
	1 %	Sodium formate	20 min	pH 4.2
	1.0 %	Sodium bicarbonate	3 x 10 min 30 min	pH 5.0
Wash twice with 200% water for 10 min				
RETANNING*	150%	Water, 35°C		
	10%	Retanning agent*	60 min	
***DIFFERENT RETANNING AGENTS**				
Experiment 1 - Control - No retanning agent				
Experiment 2 - Acrylic polymer syntan				
Experiment 3 - Phenol naphthalene formaldehyde condensate				
Experiment 4- Phenol formaldehyde syntan				
Experiment 5 - Melamine formaldehyde syntan				
Experiment 6 - Glutaraldehyde based syntan				
Experiment 7 - Styrene maleic anhydride syntan				
Experiment 8 - Sulphone based syntan				
Experiment 9 - Heterocyclic N-methylol based syntan				
FATLIQUORING/DYEING	3 %	Acid black dye		
	10 %	Water, 35°C	60 min	
	6%	Neats foot oil based fatliquor	60 min	
	1.0%	Formic acid, 85%	3 x10 min	
	10%	Water, 35°C	30 min	pH 3.5

The sample leathers were rinsed in water and piled over night followed by setting, drying, staking, trimming and buffing.

However, each of the energy term can be split into polar Lifshitz-Vander Waals and polar acid-base components. The approach of Van oss et.al.[4,5] to evaluate the surface energies, have been used. According to this approach, surface free energy of a phase is expressed as a sum of polar Lifshitz-Vander Waals and polar acid-base components.

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (2)$$

[γi in eqn (2) is also denoted as γS, γ_i^{LW} is denoted as γS^d (dispersive components) and γ_i^{AB} is denoted as γS^p (polar component)].

The acid base component results from an electron donor (Lewis base) γS^+ and an electron acceptor (Lewis acid) γS^- and is given as

$$\gamma_i^{AB} = 2(\gamma_i^- \gamma_i^+)^{1/2} \quad (3)$$

Therefore, the total interfacial energy between phases i and j are (i and j denote any two phases respectively)

$$\gamma_{ij} = \gamma_i^{LW} + \gamma_j^{LW} - 2(\gamma_i^{LW} \gamma_j^{LW})^{1/2} + 2[(\gamma_i^- \gamma_i^+)^{1/2} + (\gamma_j^- \gamma_j^+)^{1/2} - (\gamma_i^- \gamma_j^+)^{1/2} - (\gamma_i^+ \gamma_j^-)^{1/2}] \quad (4)$$

Quantitatively surface roughness ($\Delta\theta$) is the contact angle hysteresis (variability of θ as shown in scheme 1) and is the result of the system under investigation with inhomogenities. Work of adhesion is the attachment of substance A adhering to solid B. The work of adhesion could be defined in terms of Young's equation $-\Delta G_{SL} = Wa = \gamma s^0 + \gamma_{LV} - \gamma_{SL}$ and the Young-Dupre relation[7] $-\Delta G_{SL} = Wa = \Pi_{eSV} + \gamma_{LV}(1+\cos\theta)$. The film pressure is neglected ($\Pi_{eSV} = 0$), hence $-\Delta G_{SL} = Wa = \gamma_{LV}(1+\cos\theta)$, where Wa is work of adhesion.

The surface charge of the skin is one of the most important factors determining the behaviors of the leather in wet operations such as retanning, fatliquoring and coloring[8]. The dyeing processes are particularly susceptible to the nature and magnitude of the charge[9]. Thus a variety of intensities and hues, as well as different degrees of penetration are possible. Leather acquiring a positive or negative charge will also depend on the type of fat liquor used[10]. The charge of fatliquor is usually negative, as the most common water-soluble fatty substances are soaps or sulphates. The water-solublising group is either the carboxyl or sulphonic group, and both convert the fatty radical with which they have reacted, into an anion. However, syntans also influence the surface charge of the leather. The physical performance of the leather is altered based on the ionicity of retanning systems.

Studies and measurements of contact angles of liquids on solids have great technological importance. Retanning using syntans is important in improving the compaction of leather and also to reduce the aniosotrophicity of leather with respect to the feel of the substance in different regions of the leather and also from one leather to another made from the same lot. There are a wide variety of syntans used in leather making and each one of them is claimed to impact certain functional property to the leather. It is of prime importance to know how each of the syntans behaves in influencing the surface characteristics of the leathers with respect to its charge, roughness and work of adhesion. An earlier work on surface energy of electrolyte solutions at air-liquid and solid-liquid interface, Maheshwari etal., suggested that electrostatic field on solid surfaces due to the presence of various ions is generally reflected in γ_{SL}.[11] Further a number of studies on the induced effects on the interfacial energies of the solid-liquid interface have been reported[12,13]. Hence in the present study an attempt was made to relate the surface interactions on leather surface in the presence of water, DMSO and hexadecane with that of the solid-liquid interfacial energy γ_{SL}.

The surface of the crust leathers is expected to be altered in terms of acidity, basicity, surface roughness. In the present study an attempt has been made to study the influence of different retanning agents on the surface characteristics of the leathers by measuring the changes in surface properties like surface free energy (γ_S), acidity (γ_S^+), basicity (γ_S^-), polarity (γ_S^p), surface roughness ($\Delta\theta$) and work of adhesion (Wa)

EXPERIMENTAL

Reagents and Chemicals

Basic chromium sulfate (BCS) and post tanning and finishing chemicals used for the manufacture of crust and finished leathers are of technical grade. Other chemicals used for the study are of analytical grade.

Experimental Trials

Conventional chrome tanned goat leathers (27 pieces) from a same lot of similar weight range, size and grade were selected for the study. The leathers were sammed and shaved to 1.0 mm thickness. Three samples, cut into 30 X 30 cm^2 size samples from the butt region were taken for each trial and the quantity

TABLE II
Finishing Process of Control and Retanned Leathers

Crust Material: Goat Dyed Crust					**Finish: Resin Pigmented Black**
Products	**Coats***				**Procedure**
	I	II	III	IV	
Cationic Oil Ground	50				Coat I: 1x Spray, Stone Polish
Cationic Wax	50				Coat II: 4x Spray
Cationic PU	50				Coat III: 2x Spray, Finiflex 100°C/full pressure
Cationic Pigment - Black	50				Coat IV: 1x Spray
Water	800	480	500	950	
Pigment - Black		80			
Wax Emulsion		40			
Waxy Soft Protein Binder		30			
Poly Urethane Emulsion		50			
Medium Soft Resin Binder		150			
Soft Resin Binder		150			
Filler		20			
Water Based CAB Lacquer			500		
Feel Modifier - Wax Based				50	

* - Numbers mentioned are g/L of season coat

TABLE III
Contact Angles (θ) of Water, DMSO and Alkane with Leather

Sample	Water	DMSO	Alkane
Control - No retanning agent	61	2	0
Acrylic polymer syntan	38	0	11
Phenol naphthalene formaldehyde condensate	61	0	0
Phenol formaldehyde syntan	83	0	3
Melamine formaldehyde syntan	68	7	0
Glutaraldehyde based syntan	69	1	2
Styrene maleic anhydride syntan	67	8	11
Sulphone based syntan	63	0	0
Heterocyclic N-methylol based syntan	69	11	0

of chemicals offered for the post tanning process was based on shaved weight. The samples were processed into upper leathers as per the process described in Table I. The effect of syntans (retanning agents) on surface charge, surface free energy, surface roughness and work of adhesion of dyed crust were studied. The samples were finished as per the process described in Table II. Finish Adhesion and fastness to rubbing was carried out on finished leathers

Measurement of Static Contact Angle:

The contact angles of water, DMSO and hexadecane at the leather surface were measured using a custom built instrument. Measurement of contact angle was done by projecting the image of the liquid drop on a leather surface and onto a screen and the contact angle was accurately measured. The experimental error in θ was ±0.1 degree. When the drop of liquid is resting on solid surface like leather, the drop which forms a contact angle, may be considered as resting in equilibrium by balancing the three forces involved namely the interfaced tensions between solid liquid (SL), liquid vapor (LV) and solid vapor (SV). The angle within the liquid phase is known as contact angle θ or wetting angle[14] of the leather. Each value of θ was the mean of at least 3 measurements taken at each point of the three numbers of leather surface. Further, at least 5 different locations were taken on the surface and the average of 15 measurements were then used.

Measurement of Surface Roughness

Roughness of the leather surface was measured by the formula $\Delta\theta = | \theta a - \theta r |$, Where, θa is advancing angle and θr is receding angle as shown in scheme 1. The hysteresis (change in θ) formed due to inhomogenity of the leather surface was measured using static contact angle.

Measurement of Work of Adhesion

The work of adhesion can be defined from Young's equation and Young-Dupre relation[7], $Wa = \gamma_{LV} (1+ \cos\theta)$, where Wa is work of adhesion that was measured using contact angle.

Measurement of Adhesion of Finish

Samples from all the retanned leathers of appropriate size (5 x 14 cm) were cut from the official sampling position[15] and were tested according to IUF 470[16].

Determination of Fastness to Wet and Dry Rub

Samples from all the retanned leathers were tested according to IS 6191 - 1971 (LF: 10).[17] This method uses a SATRA Crock meter.

RESULTS AND DISCUSSIONS

Contact Angle and Surface Parameters of Leather

From the contact angles of the water and two liquids, DMSO (medium non-polar) and hexadecane (non-polar) made with leather surfaces as shown in Table II, surface polar component (γS^p), dispersive component (γS^d), acidic and basic components (γS^-, γS^+) of the surface energy (γS) of the film were determined. The pores, crevices and capillaries contributed by different retanning agents on the leather surface reflect the extent of roughness that was measured. Schwartz and Garoff[18] and Morrow[19] used capillary rise concepts to describe hysteresis due to surface roughness. Timmons and Zismann[20] attributed hysteresis to micro porosity of the solids, because they found hysteresis to depend on the size of the liquid molecules or associated cluster of molecules. The measurement of a single static contact angle to characterize the interaction is no longer thought to be adequate. For any given solid/ liquid interaction there exists a range of contact angles. The work of adhesion between a liquid and a solid is actually the Gibbs free energy change per unit area upon separating the two surfaces. Work of adhesion is the work required to pull apart 1 cm^2 interface of solid and liquid. Good wetting will be sufficient to generate a good adhesive bond between two substances. Adhesion to an abraded or rough surface is improved because of microscopic or sub microscopic crevices and pits into which a coating could penetrate and even gain a kind of mechanical foothold. An abraded surface with many crevices, pits and irregularities has a higher surface area than the unabraded, smooth surface. Usually larger surface area of contact facilitates adhesion.

The surface related parameters viz., surface energy, acidity, basicity, roughness and work of adhesion of different retanned leathers has been calculated based on the contact angles that the leathers made with different liquids, viz., water, DMSO and

TABLE IV

The Surface Free Energy (γS), Acidity (γS^+), Basicity (γS^-), Polarity (γS^P), Surface Roughness ($\Delta\theta$) and Work of Adhesion (Wa) of Control and Different Retanned Leathers.

Sample	γS^d mN/m	γS^P mN/m	γS mN/m	γS^+ mN/m	γS^- mN/m	Surface roughness $\Delta\theta = \theta a - \theta r$			Work of Adhesion (W_a) mJ/m²
						θa	θr	$\Delta\theta$	
Control - No retanning agent	27.04	18.31	45.35	5.11	13.02	64	126	62	103.85
Acrylic polymer syntan	26.55	26.63	53.18	5.35	33.15	73	122	49	93.31
Phenol naphthalene formaldehyde condensate	27.04	16.32	43.35	5.12	12.99	87	120	33	75.98
Phenol formaldehyde syntan	27.01	4.60	31.61	5.13	1.03	65	111	46	102.71
Melamine formaldehyde syntan	27.04	12.73	39.77	4.98	8.12	75	104	29	90.89
Glutaraldehyde based syntan	27.01	12.24	39.25	5.13	7.30	75	110	35	90.89
Styrene maleic anhydride syntan	26.55	13.48	40.04	5.17	8.78	68	111	43	99.25
Sulphone based syntan	27.04	8.33	35.37	5.12	3.39	70	110	40	96.89
Heterocyclic N-methylol based syntan	27.04	12.16	39.20	4.92	7.70	64	109	45	103.85

hexadecane are listed in Table IV. By observing the values obtained, it is seen that the surface free energy (γS) is found to be highest for acrylic polymer retanned leathers (53.18 mN/m) and least for phenol based retanned leather (31.61 m N/m). For all the other samples, the γ_S values are between 35 and 45 mN/m showing the surface energy does not dramatically change in the leathers. However γ_S^P show larger deviations. The γS^P values are high for acrylic polymer (26.63 m N/m) and least for phenol based syntan (4.60 m N/m). Acrylic polymer seems to be highly polar which is indicated from the high γS^P values.

The acidic component (γS^+) is more or less the same for all the retanned systems with the values ranging from 4.9 to 5.4 m N/m. γS^-, where as the basicity indicator shows gradation. Here the values are in the following increasing order with values going from 1.03 - 33.15 m N/m. Phenol retanned leather < sulphone retanned leather < glutaraldehyde retanned leather < heterocyclic N-methylol retanned leather < styrene maleic anhydride retanned leather < phenol naphthalene condensate retanned leather < control (without retanning) < acrylic polymer retanned leather, the basicity scale ranging from 0 to 35 m N/m. Surface roughness of the crust leathers influence finishing and surface related parameters. With respect to $\Delta\theta$ values, control has the highest values (62°). The values are in the following increasing order with values ranging from 30° to 65°. Melamine retanned leather< phenol naphthalene condensate retanned leather < glutaraldehyde retanned leather < sulphone retanned leather < styrene maleic anhydride retanned leather < heterocyclic N-methylol retanned leather < acrylic retanned leather < control. Similarly, the work of Adhesion (Wa) values is in the following increasing order. Phenol naphthalene retanned leather < Melamine and glutaraldehyde retanned leather < acrylic retanned leather < sulphone retanned leather < styrene maleic anhydride < heterocyclic N-methylol retanned leather and control leather.

Meaningful interpretations of absolute values of surface energy can be carried out only when sampling is done on a large number of skins and different retanning combinations. However, the aim of the present study is to explore the effects of different retanning agents. Hence in the present analysis, difference in the surface energies between the control and the differently retanned leathers has been used in various plots. In order to get a clear trend of all the surface characteristics of different leathers, it was necessary to draw a correlation among various parameters as described in Figures 1, 2, and 3. Hence correlation plots are drawn by relating γS and γS^-, $\Delta\theta$ and Wa; $\Delta\theta$ and γS^P.

Correlation between Surface Free Energy (γS) and Basicity of Surface (γS^-) of Leathers Retanned with different Syntans

Figure 1 describes the surface free energy and basicity for various retanned leathers as calculated form the static contact angle measurements. Acrylic polymer retanned leather has highest surface free energy and highest basicity compared to all the other retanned leathers. The least in the series (phenol based retanned leather) has the lowest surface free energy and basicity. Control and phenol naphthalene condensate retanned leathers show γS and γS^- in the similar range. Leathers retanned with melamine, glutaraldehyde, styrene maleic anhydride and heterocyclic N-methylol can be grouped together having

TABLE V
Finish Adhesion and Fatness to Rubbing of Different Retanned Leathers

Sample	Finish Adhesion	Crust Leathers		Finished Leathers	
		Wet rubbing	Dry rubbing	Wet rubbing	Dry rubbing
Control - No retanning agent	7.6±0.34	4.5±0.25	5	4±0.25	4±0.25
Acrylic polymer syntan	8.6±0.28	5	5	4.5±0.5	4.5±0.25
Phenol naphthalene formaldehyde condensate	6.82±0.42	4±0.5	5	3±0.5	4±0.25
Phenol formaldehyde syntan	5.48±0.21	4±0.25	5	3±0.25	4±0.25
Melamine formaldehyde syntan	6.36±0.13	4.5±0.5	5	3±0.25	4±0.25
Glutaraldehyde based syntan	6.32±0.27	4.5±0.25	5	3±0.25	4±0.25
Styrene maleic anhydride syntan	6.42±0.18	4.5±0.5	5	3±0.25	4±0.25
Sulphone based syntan	6.12±0.43	4±0.25	5	3±0.25	4±0.25
Heterocyclic N-methylol based syntan	6.23±0.26	4.5±0.25	5	3±0.25	4±0.25

surface free energy lower than control. Sulphone retanned leather form another category having surface free energy greater than phenol based retanned leather. Highest surface energy and basicity of leather will influence the adhesion of finish to leather and in turn reflect on the wet and dry rub fastness of the finished leathers.

Correlation between Surface Roughness ($\Delta\theta$) and Work of Adhesion (Wa) of Leathers Retanned with different Syntans

Figure 2 relates the surface roughness and work of adhesion for various retanned leathers calculated form the contact angle, polarity, basicity and surface energy values. For control sample, $\Delta\theta$ was found to be high. This indicates that surface of leather without any syntan is rougher. This could be easily explained by the fact that the control leather is not fuller and syntans bring in filling effect to leather, which in turn can reduce the crevices and pits in the leathers. Melamine, glutaraldehyde and phenol naphthalene condensate retanned leathers have the lowest $\Delta\theta$ values, which indicate that they are better filling syntans. Glutaraldehyde retanned leathers show gradation for fullness in leathers. It is well known that glutaraldehyde self polymerizes and could have deposited on the grain exhibiting higher smoothness in the leathers. Styrene maleic anhydride, phenol based, heterocyclic N-methylol and sulphone retanned leathers can be grouped together to have slightly lower $\Delta\theta$ when compared to control and to have smoothness less than that of phenol naphthalene and glutaraldehyde retanned leathers. Sulphone based and styrene maleic anhydride retanned leathers will have better filling characteristics in leather than phenol and heterocyclic N-methylol syntan based retanned leathers among the same group. From $\Delta\theta$ values fullness of acrylic retanned leathers is lower than phenol based and heterocyclic N-methylol retanned leathers. Melamine retanned leathers, glutaraldehyde retanned leathers and phenol naphthalene condensate retanned leathers have similar surfaces. Hence they will contribute to more fullness in leather and are found to have significant smoother surfaces than control. The work of adhesion is the highest for heterocyclic N-methylol retanned leathers comparable to control. Phenol based retanned leathers also show higher values. These leathers have lower smoothness as seen from the roughness values. Hence, more energy is required to pull the finish out of the leather. The lowest of the values of work of adhesion is for phenol naphthalene condensate, melamine and acrylic polymer retanned leathers as they have lower Wa values. Also these leathers have more smoothness as seen from the roughness values, hence these leathers contribute to maximum fullness in leather and less energy is required to pull the finish out of the leather.

Correlation between Surface Roughness ($\Delta\theta$) and Polarity (γ^{SP}) of Leathers Retanned with different Syntans

Figure 3 describes the surface roughness and polarity for various retanned leathers. Control has the highest $\Delta\theta$ value indicating that the surface is rougher. Acrylic polymer retanned leather has highly polar surface, when compared to control and has a less smooth surface (as compared to melamine retanned leather). This indicates that the acrylic retanned leather will adhere, finish better to leather better than control as the polarity of the surface is lower for control even though surface is rough. Roughness alone cannot directly influence finishing because in control piece one can have variations in pore sizes, pore size distribution and surface charge. Phenol based retanned leather on the other hand is an extreme, which has the least polar values when compared to acrylic polymer retanned leather (highest polar values) and the surface is less smoother compared to control. Phenol retanned leather is only little polar when compared to Heterocyclic N-methylol retanned leather (higher Wa) but very less when compared to control. Sulphone based retanned leather lies intermediate between phenol based retanned leather and heterocyclic N-methylol based retanned leather. Styrene maleic anhydride retanned leather has lesser $\Delta\theta$ values when compared to control showing that it is slightly smoother but is less polar when compared to acrylic polymer retanned leather. For phenol naphthalene condensate retanned

leather there seems to be a drastic decrease in $\Delta\theta$ values. Surface is smoother and the polarity is equal to control. For glutaraldehyde retanned leathers $\Delta\theta$ value is less. Surface is smooth. The polarity of the leather is lower than the control. Resin melamine retanned leather has the smoothest surface of all the leathers because of less $\Delta\theta$ value but γ_S^p value is intermediate between the highest polar component (acrylic polymer retanned leather) and phenol based retanned leather, which is lowest in polarity.

Influence of Syntans on the Fastness and Adhesive Properties of Leather

The fastness to wet and dry rub and finish adhesion of different retanned leathers before and after finishing are given in Table V. It is basically mistaken to assume that the finish formulation alone directly influences the rub fastness and finish adhesion of the final leathers. But there are other important factors like surface roughness, polarity and work of adhesion, which have greater impact on the rub fastness of leather. Therefore, for rub fastness purposes, a comparison was made with a control leather without any retanning, which has a rougher surface ($\Delta\theta$ was high), but basicity γ_S^- was low and work of adhesion Wa was the highest. Leather with rougher surface can be expected to exhibit better rub fastness. However the leather (acrylic retanned leather) with slightly lower roughness and work of adhesion but with better polarity and basicity had the best of the rub fastness properties when compared to control. Phenol retanned leather exhibited lowest fastness. Also all the other leathers had comparatively lower rub fastness than acrylic retanned leathers. This goes with the assumption that leathers with strong polarity not only wets the leather faster buts also anchors better to finish. The results are synonymous to the adhesion of finish to leather as given in Table V. Therefore the adhesion of finish to crust also plays a decisive role based on charge than on the roughness of the leather. Hence it is often observed that finishes well anchored to leather exhibit better rub fastness as seen in this also. From Table V, it is evident that adhesion of finish to different retanned leathers is slightly lower than acrylic retanned and control leathers. Different retanned leathers, in general exhibited similar trend for rub fastness and adhesion. The effect on ageing on the rub fastness properties measured after ageing for 6 months has been found to be similar to the values before ageing.

From the interpretations discussed we can conclude that the different types of syntans used in the retanning process will have definite surface characteristics and the surface properties of these retanned leathers, influence the finish properties of the final leather. An understanding of such phenomenon is essential to understand the finishing process as the crust carries a surface charge or polarity, surface energy, roughness and work of adhesion and these properties directly influence the finish properties of leather. Hence the study of these properties will assist the leather technologists to have thorough understanding of the crust and develop finishes that suit their needs and a knowledge base to improve the finish properties of leather.

CONCLUSIONS

The study shows that the surface energy value, made of two components, the dispersive and polar values, can act as good indicators to study the surface behaviour and the degree of surface charge of the leather. Further, the polar component being more sensitive of the two, it acts as a clear measure of the charge contributed by different retannins to leather and has been used to study the variation of surface charge from different retannins. The present investigation shows that the phenol based retanned leather has a low surface energy value, compared to acrylic polymer retanned leathers which has highest values. Acrylic polymer retanned leathers are highly polar. Surface of leather without syntan is rougher. Melamine and acrylic polymer retanned leathers have smoother surfaces and contribute to more fullness in leather. The surface charge values that show excessively high positive charge in the leather do not combine with the finish properly. In the case of excessively low positive charge, the finish may penetrate into the leather and lose its part of its hiding effect. From the surface energy values of leathers with different retanning agents, it can be inferred that higher the polarity and lower surface energy, higher will be the adhesion for finishing. This is because when the retanning agents contribute to high pH, the leather is slightly cationic or neutral. Hence the leathers (acrylic retanned leather) with higher polarity and basicity, moderate roughness and work of adhesion, good adhesion of finish was observed. Therefore the adhesion of finish to crust also plays a decisive role based on charge than on the smoothness of the leather. Hence it is also observed that finishes well anchored to leather exhibited better rub fastness.

This observed difference could be an added advantage in selecting the right type of retanning system for desired finishing system. Thus a high quality finishing system can be ensured by the choosing the right type of retanning systems that contribute to the surface properties of the leather, which will improve the cutting value of leather for better value addition. Thus a quantification of surface charge density through the surface energy, study of surface roughness and work of adhesion can become innovative tools of the future leather processing.

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