Performance of Sulfonated Dimeric Malenised Soya Fatty Acid as a Leather Fatliquor

by

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Abstract

A change of molecular structure improves the surface-active efficiency of new generation gemini surfactants. As a result, it was confirmed that the dosage could be reduced considerably in industrial applications as performance chemicals, leading to economically quantifiable benefits. The performance of newly synthesized gemini surfactant based sulfonated gemini malenised soya fatty acid bridged with butane diol was evaluated as a leather fatliquor. The chemical parameters of the fatliquors were analysed and tested on leather. The properties imparted by the fatliquor to leather were studied qualitatively and quantitatively. SEM studies of the treated leathers revealed better penetration of the gemini surfactant based fatliquor compared to the control. Results were correlated in terms of emulsification power, zeta potential and particle size of the surfactants; and likewise found to be better than the conventional surfactant. The surface energy was calculated for the fatliquors and found to be equal.

Resumen

Un cambio en la estructura molecular mejora la eficiencia activa sobre la superficie de una nueva generación de tensoactivos Géminis. Como resultado, se confirmó que la dosificación se podría reducir considerablemente en aplicaciones industriales de estos productos químicos de alto rendimiento, conllevando a beneficios económicos cuantificables. El rendimiento de estos nuevamente sintetizados tensoactivos gemelos basados en ácidos grasos sulfonados de soja maleizada y puenteada con butano diolizado fueron evaluados como engrases para cuero. Los parámetros químicos de los engrases fueron analizados y probados en cueros. Las propiedades impartidas por los engrases a cueros fueron estudiadas cualitativamente y cuantitativamente. Estudios microscópicos electrónicos por barrido [SEM] de los cueros revelaron aumentada penetración de los tensoactivos engrases Géminis en comparación al control. Los resultados fueron correlacionados en base a poder emulsionante, potencial zeta y tamaño de las partículas del tensoactivo; los cuales se encontraron que superaban los del tensoactivo convencional. La energía superficial se calculó para los engrases y encontró que son iguales.

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INTRODUCTION

Leather is a unique flexible sheet[1] of material somewhat analogous to textiles, strong, durable, supple, soft, warm and porous. It is mainly a fibrous protein known as collagen and is composed to one continuous network of fibers. There are about 25 operations in the process of converting hides and skins into leather. Fatliquoring is the last wet chemical process[2] in the leather making process and is the application of mixture of oils and emulsifiers to leather. The process lubricates the leather fibres, coating them with substances that reduce the internal friction. As a consequence, the leather acquires softness and a degree of water proofing.[3] It was shown that the amount of surfactant that must be applied to leather to achieve the desired product properties exceeds by ten fold the amount calculated to coat the collagen fibrils with a monomolecular layer, although these properties were retained when most but not all the applied material was extracted.[4] Current methods for lubricating leather, however, employ oils and surfactants that have been known to destabilize collagen fibers and to impair the mechanical properties of leather.[5] The important factors to the fatliquoring mechanisms [6] are charge on the leather, emulsion stability, particle size distribution of an emulsion, ratio of emulsifier to neutral oil, viscosity and interfacial tension of oils. Softness depends on the ability of the oil to be emulsified and carried into the leather.[7]

In our earlier work, we have synthesized a new sulfonated gemini malenised soya fatty acid surfactant, having two hydrophilic and two hydrophobic groups having 1,4: butane diol as the spacer.[8] We have taken up this present work to substitute the new surfactant with reduced dosage in place of a conventional surfactant in a fatliquor formulation. Chemical parameters of the fatliquors were analysed and tested on leather. The properties imparted by the fatliquor to leather were studied qualitatively and quantitatively. SEM studies of the treated leathers were carried out to study the morphology and penetration of fatliquor. Results were correlated in terms of emulsification power and zeta potential of the surfactants. The surface energy was calculated for the fatliquors.

EXPERIMENTAL

Materials and Methods

Formulation of fatliquors

Fatliquors were prepared by taking a mixture of vegetable oils (25%), mineral oil (5%), chloroparaffin sulfonate[9] (15%), neutralizing agent (3%) and sulfonated surfactant (12%). The composition was adjusted to 100 % using water. In the present study, the conventional sulfonated surfactant was replaced by the synthesized gemini surfactant without further purification by keeping all the other ingredients and conditions identical. In the original fatliquor (FL R), the sulfonated surfactant was kept at 12%, whereas sulfonated dimeric surfactant was substituted at 8% in the first fatliquor (FL 1) and 4% in the second product (FL 2).

Synthesis of sulphonated gemini surfactant

Soya fatty acid was reacted with maleic anhydride in presence of para toluene sulphonic acid to form malenised soya. Malenised soya was reacted with 1,4-butanediol to form gemini surfactant. and the molecular structure was given in Figure 1. The dimer was sulphonated using sodium bisulfite to yield sulphonated gemini surfactant. The surfactant was characterized by spectral techniques and surfactant properties. Eventhough quite a number of gemini surfactants reported in the literature, the synthesized new sulphonated gemini surfactant prepared by the above mentioned route was not reported so far. The results of the synthesis and the characterization will be published elsewhere.

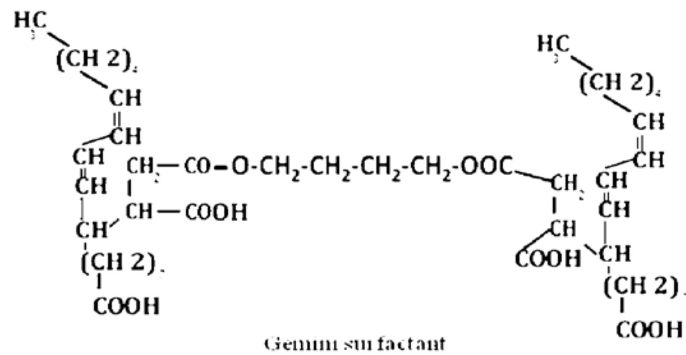

Figure 1

% Water content was analysed as per Indian Standards 548:1964. pH was measured using pre-calibrated standard LABINDIA make pH meter. Color of the fatliquors were measured with Lovibond PFX 195 Tintometer. The fatliquors were applied on wet blue cow leather and compared with the original fatliquor separately as a control. Fatliquoring process adopted and the experimental details were given in Table I.

Leather characteristics such as feel, inner softness, grain touch, stretch and bleaching were measured visually by different leather technologists, qualitatively and standard deviation method was applied to arrive at the composite results. Tensile strength was measured using PROLIFIC tensile strength machine. Grain and bursting strengths were measured through PROLIFIC elastometer. SEM analysis of the dried leather samples were carried out using JEOL 400 microscope after spin coated with gold.

Emulsification power[10] was determined as the separation time measurement. Zeta potential was measured using Zetasizer 2000, model DTS 5202, from M/s Malvern Instruments Limited, UK. Surface tension was measured using KRUSS tensiometer K100 (KRUSS GmbH, Hamburg) at ambient

TABLE I
Leather fatliquoring process

Products	% Used	Duration in minutes	Remarks
Water Wetting agent	100 1.0	30	Drain / Wash / Drain
Water Formic acid	100 0.75	20	Check pH (3.2) Drain out
Water Basic chromium sulphate	100 4.0		
Chrome syntan Fat emulsion Sodium formate Sodium bicarbonate	2.0 0.25 1 .0 1.0	60 10 2 equal feeds at the interval of 10 minutes and run for 30 minutes	Check pH (4.0) Drain / Wash / Drain
Water Neutralisation agent Sodium formate Sodium bicarbonate	100 2.0 1.0 1.0	30 10 2 equal feeds at the interval of 10 minutes and run for 30 minutes	Check pH 5.2, Drain / Wash / Drain
LHS : RHS **FL (1) / FL (2) :** **FL (R)**	8.0	60	
Formic acid	1.5	2 equal feeds at the interval of 10 minutes and run for 30 minutes	Check exhaustion Drain / Wash / Drain/ Pile over night/ Next day single setting, Hook to dry, Stake.

temperature by ring balance method.[11] Contact angle was determined using KRUSS tensiometer K 100 by sorption measurements according to the Washburn method [12]. Particle size of the surfactants was measured using spectrex laser particle counter, (PC-2200^R), size range 1-100 microns.

RESULTS AND DISCUSSION

Chemical analyses of FL R, FL 1 and FL 2 fatliquors
Prepared fatliquors FL R, FL 1 and FL 2 were analyzed for chemical parameters. Colour in lovibond gardener scale found to be 12 with clear clarity. % Water was 40.0 and pH was 8.0. Fatliquors using hard water emulsions prepared upto 2000 ppm of calcium chloride were stable.

Leather properties
Wet blue cow leathers were treated with the prepared fatliquors using FL 1 Vs FL R and FL 2 Vs FL R. After drying, the leathers were evaluated qualitatively and quantitatively. Detailed results were given in **Tables II and III.**

TABLE II
Organoleptic properties of FL 1 / FLR and FL 2 / FLR

Scale of grading: 1: Very Poor, 2: Poor, 3: Good, 4: Very Good and 5: Excellent

PROPERTIES	FL 1	FL R	FL 2	FL R
FEEL	4.8	4.7	4.7	4.6
INNER SOFTNESS	4.8	4.7	4.7	4.6
GRAIN TOUCH	4.8	4.8	4.7	4.7
STRETCH	4.8	4.7	4.6	4.6
BLEACHING	4.7	4.7	4.6	4.6

TABLE III
Physical testing results of FL 1 / FLR and FL 2 / FLR

TESTINGS	FL 1	FL R	FL 2	FL R
TENSILE STRENGTH (Kg/Cm^2)	108.2	105.9	145.3	114.8
Standard Deviation	3.8	3.3	4.1	3.3
ELONGATION (%)	68	67	82	73
Standard Deviation	1.6	1.6	1.8	1.8
GRAIN CRACK STRENGTH (Kg)	68	33	76	73
Standard Deviation	3.3	1.8	3.3	3.3
DISTENSION 1	12.9	11	12.3	12.2
Standard Deviation	1.6	1.8	1.6	1.6
BURSTING STRENGTH (Kg)	78	75	87	85
Standard Deviation	3.3	3.8	3.8	3.3
DISTENSION 2	13	12.9	12.8	12.8
Standard Deviation	1.8	1.6	1.8	1.8

The leather performance factors of the fatliquors FL 1 and FL R were compared. We could observe that the feel, inner softness,[13] stretch and bleaching were found to be very close on the scale of qualitative assessment, whereas grain touch was equal. The tensile strength and bursting strength were much closer whereas, grain crack strength was better.

When we compare the fatliquors FL 2 and FL R, it was observed that grain touch was equal, whereas the other properties like feel, inner softness, stretch and bleaching were better. The tensile strength was found to be better compared to grain crack strength and bursting strength, which were closer. From all the results, FL 2 was a better fatliquor where we could enhance the leather performance properties even with 66% dosage reduction using the newly prepared gemini surfactant.

SEM studies of grain pattern of leathers fatliquored with FL 2 and FL R were given in Figures 2 and 3, at a magnification of X 1000. Fiber splitting of the grain of both the leathers were very well observed. In the case of FL 2 corresponding to the gemini surfactant, the penetration was still better than the other one, which was established by the qualitative and quantitative assessment of leather parameters.

Leather parameters were derived from the fibril bundles to distort and slip when the stress was applied. To get the better fiber bundle splitting, the structure should not stuck together by the adhesions created during drying and lubricant should be able to allow the fibers to slide over one another.[14] These parameters were achieved by the addition of fatliquors. The effectiveness of fatliquoring depends on the degree of the penetration of the fatliquor, which was predominated by the surfactant present in the system. In our study, conventional fatliquor as a control and the new gemini surfactant based fatliquor were sulfonated surfactants. But carrying the neutral oil into the deep of the leather containing fibrils was better in the case of gemini surfactant because of its higher surface activity.

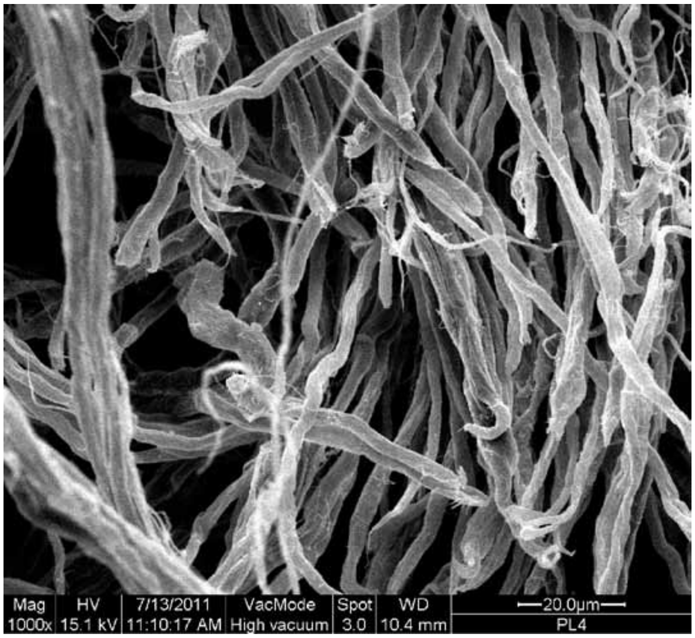

Figure 2: Scanning electron microscopic photograph [x 1000 magnification] of grain surface of the leather fatliquored using FL 2, containing sulfonated dimeric malenised soya fatty acid surfactant

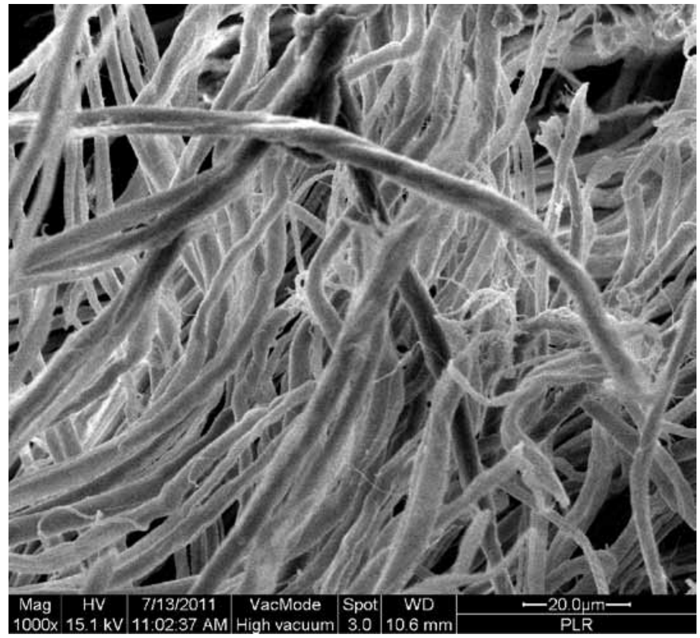

Figure 3: Scanning electron microscopic photograph [x 1000 magnification] of grain surface of the leather fatliquored using FL R, containing conventional sulfonated surfactant

Addition of gemini surfactant to the lubricating oil decreases effectively the interfacial tension between oil and water in order to penetrate lubricating emulsion, which resulted in deeper penetration showing higher performance. Also, the gemini surfactants destabilize collagen fibers and impairs the mechanical properties to leather because of the higher hydrophilic nature. The solubility was better to form a stable solution. The gemini surfactants besides having the property of being able to emulsify and disperse fats and oils, posssess the capacity of binding to proteins[15] through electrostatic and hydrophobic interactions.

It was also to be noted that the quality of the grain surface of the treated leather depends to a great extent on the size of the hair follicles.[16] If leather processing reduces the hair follicle mouth to a small almost closed aperture, the grain surface will have a higher natural gloss.

Phase behaviour of mixed systems involving oil, water and surfactants was an important area of research in the field of surfactant chemistry[17] whose study often was found to be tedious and time consuming. In the leather application as fatliquors, surfactants were used in formulations containing mixtures of different compounds, and synergism[18] can often be observed. Synergism was defined as the condition in which the properties of a mixture were better than those attainable with the individual components separately, where the aggregation of the surfactants play a crucial role. Conventional surfactants form spherical aggregates, whereas gemini surfactants forms either thread like or rod like micelles.[19]

When the fatliquor was applied before the leather was dried, it reached the fibrils that, on drying, will remain within the cohesive domains[20] and as a result, on drying all the adhesions in the leather became weaker.

Emulsification power of the surfactants

Emulsification power results of the conventional sulphonated surfactant (1) and the gemini surfactant (2) were analyzed and given in Table IV.

TABLE IV
Emulsification power of surfactants

Parameters	1	2
	(sec)	(sec)
Emulsification power of 1% solution		
Time taken for 10 ml of aqu separation	9	19
Time taken for 20 ml of aqu.separation	16	38

Emulsification provides the surfactant ability and gives the emulsification capacity. The emulsification capacity was comparatively higher because of the presence of more hydrophilic groups in the gemini surfactant. In the present study, it was found that the emulsification power of gemini surfactant shows two fold capacity than the conventional surfactant. Gemini surfactant emulsifies the free oil available in the fatliquor to the maximum possible extent which gives better penetration and produce good absorption. In the conventional surfactant system, neutral oil available in the system would deposit on the surface of the leather due to lesser emulsification power. It was observed that the oil deposited on the fibrils of the leather[21] in the case of gemini surfactant due to higher emulsification power.

The tighter packing of the hydrophobic groups of the gemini surfactant compared to the conventional surfactant at the interface result in a more cohesive and stable interfacial film[22] which indicates the higher emulsification power. Strong interaction in the system at interfaces or in mixed micelles occurs because of more ionicity than the conventional surfactants.[23] Packing of the hydrophobic groups in the gemini surfactant at the aqueous solution – air interface was closer than that found in the conventional surfactants.

Higher emulsification capacity of the gemini surfactant than the conventional surfactant was also due to the distortion of water by hydrophobic groups.[24] In the case of Gemini surfactant, two hydrophobic groups in a single molecule were found to be more disruptive than individual chains in conventional surfactants. This in turn promotes the migration of a micelle to the air/water interface.

In the gemini surfactant, certain spacers can form hydrogen bonds with water and, therefore, reduce the unfavourable hydrocarbon-water contacts, making it easier for spacers to locate at the micelle-water interface. Furthermore, additional hydration at the level of the spacer chain should mitigate the coulombic repulsion[25] between the head groups. These contributions all act together to help gemini surfactant molecules to aggregate at a lower concentration. The surfactants with the higher emulsification property, besides having the property of being able to emulsify and disperse fats and oils, possess better capacity of binding to leather collagen through electrostatic and hydrophobic interactions.

Zeta potential

Zeta Potential applies to the electrical charges existing in liquid emulsions. Zeta Potential is a measure of charges carried by particles suspended in a liquid, measuring in millivolts, the difference in electrical charge between the dense layer of ions surrounding the particle and the bulk of the suspended fluid. The stability of the surfactant dependent upon the degree of ion absorption, and therefore, on the zeta potential. Zeta potential curve of conventional sulfonated surfactant (1) and the gemini surfactant (2) were given in Figures 4 and 5.

Zeta potential of (1) and (2) were found to be -38.4 mv, and -62.2 mv respectively. The magnitude indicates the potential stability of the surfactant. The higher value of zeta potential represents higher stability of the system. From the values, it was inferred that the conventional sulfonated surfactant was having moderate stability , compared to the gemini surfactant, which found to have very good stability.[26] This is a prime requirement of an ingredient of a fatliquor.

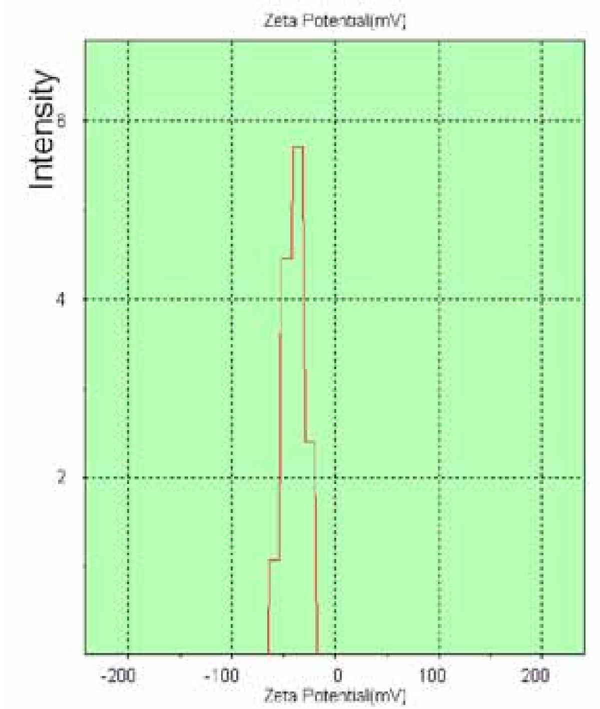

Figure 4: Zeta potential of (1)

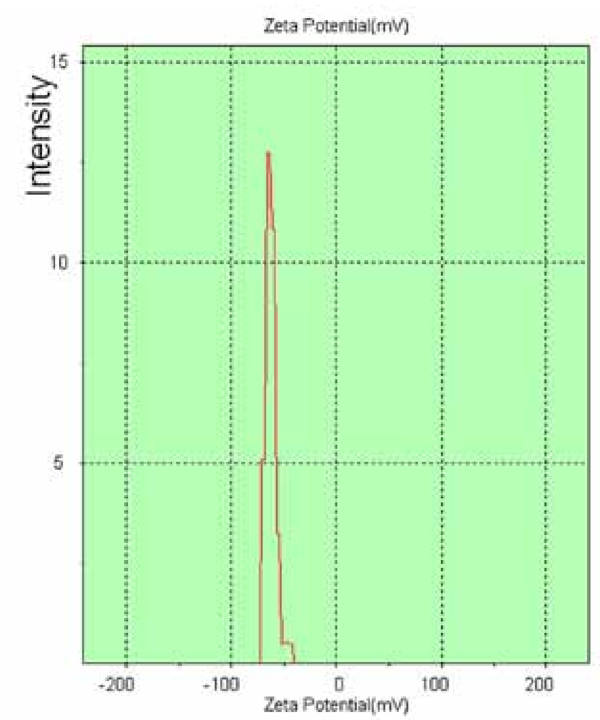

Figure 5: Zeta Potential of (2)

In the case of gemini surfactant zeta potential was higher due to the increase of surface charge density[27] of the micelles. More zeta potential lowers critical micelle concentration and thereby makes easier aggregation of micelles. CMC of (1) and (2) were found to be 0.00529 and 0.000984 mol/l. The stability of the formulations might be based on the steric effect arising from the adsorbed surfactants on the leather surface. The hydrophobic part of the surfactant was assumed to be anchored [28] on the leather surface, whereas the hydrophilic part was assumed to be directed outwards into the continuous phase of water. One approach known to stabilize an emulsion was to confer an electrostatic charge to the droplets surface which will result in droplet repulsion and less droplet coalescence.[29] Colloidal particles dispersed in a solution were electrically charged due to their ionic characteristics and dipole attributes. This charge, which can be negative resulting in anionic emulsions or positive producing cationic emulsions[30] was known in the art as the zeta potential.

Surface Energy

Young's equation [31] defines the balance of forces caused by a wet drop on a dry surface. If the surface is hydrophobic, the contact angle of a drop of water will be larger. Hydrophilicity was indicated by smaller contact angles and higher surface energy. Young's equation gives the following relation,

$$\gamma SL + \gamma LV \cos \theta_c = \gamma SV$$

where γSL, γLV and γSV are the interfacial tensions between the solid and the liquid, the liquid and the vapour, and the solid and the vapour, respectively. The equilibrium contact angle that the drop makes with the surface was denoted by θ_c. Young' surface energy model was given in Figure 6. The differences between γSV and γSL indicates the spreading or wetting of liquid on the surface. The higher value of this term indicates the surface prefers to be wetted by the liquid.

The interfacial surface tension of oil with water was very small and measuring contact angle of oil on wet leather was difficult to measure. This problem was handled by separating the oil phase and the emulsifier phase from the fatliquor and applying the young's equation. The determination of contact angles over wet leather was not practicable due to the fact that the leather contains both hydrophilic and hydrophobic regions. These experiments were performed on two different surfaces.

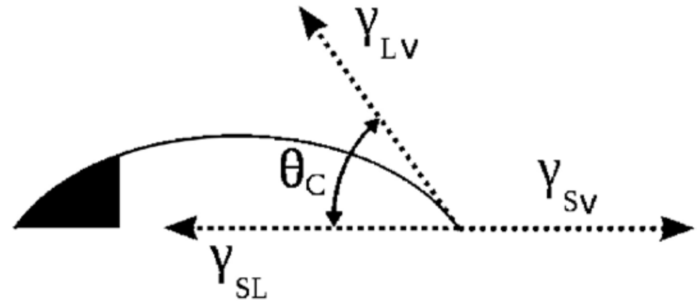

Figure 6: Young's surface energy model

That are extremely hydrophobic (Teflon) and extremely hydrophilic (Glass) surfaces.

The important characteristics of a liquid surfactant was its ability to freely spread over the surface of the object being experimented. Surface energy was quantified in terms of the forces acting on a unit length at the solid-air or the solid-liquid interface.[32] Wettability of a material was its tendency to make liquids spread out over its surface and was the direct function of surface energy.[33] Higher the surface energy of a material, the more the liquid will spread out over the surface.

Surface energy values of the fatliquors FLR and FL 2 were calculated after the separation of the oil and surfactant components. Results were given in Table V. Wetting efficiencies of FLR and FL 2 were found to be closer, and this explains the equal performance of these two fatliquors.

The adhesive forces[34] between the fatliquor and the leather will compete against the cohesive forces of the fatliquor. Fatliquors with weak cohesive bonds and a strong adhesive forces to leather will tend to spread over the material. Fatliquors with strong cohesive bonds and weaker adhesive forces will tend to form droplet up when in contact with the leather. Fatliquor will fill the voids in the leather until an opposing force balances the capillary pressure.

Performance in terms of surface energy of a fatliquor based on gemini surfactant than a conventional surfactant was due the geometrical shape of the molecules. In the gemini surfactant, the monomer of two molecules have been chemically linked

TABLE V
Surface energy values of fatliquors

Component	Surface tension (mN/M)	Contact angle – glass (°)	Contact angle – Teflon (°)	Surface energy – glass (mN/M)	Surface energy – Teflon (mN/M)
Oil of FLR	20.93	4.3	29.3	20.9	18.3
Surfactant of FLR	23.7	7.7	24.2	23.5	21.6
Oil of FL2	23.66	3.5	35	23.6	19.4
Surfactant of FL 2	26.9	11.3	24.8	26.4	24.4

by a spacer which leads to changes in the physical and chemical properties.[35] One of the main effects of introducing the spacer was to impose an additional geometrical constraint on the packing of surfactant molecules and therefore, to influence their aggregate shape. The dependence of the specific area of gemini surfactant at the air/water interface on the spacer was also important for the activity. In the present study, we have used short spacer, which will lead to large packing parameter, and may account for the formation of preferred micelles. Also, the hydrophobic repulsion leads to shorter end-to-end distances and therefore to smaller specific surface area. The geometrical effect of the spacer, the interaction among the surfactant monomers and the conformational entropy of the spacer plays an important role on the surfactant activity.

Particle Size

Particle size is a notion introduced for comparing dimensions of liquid particles as droplets. Size distribution analysis of gemini surfactant was given in Figure 7.

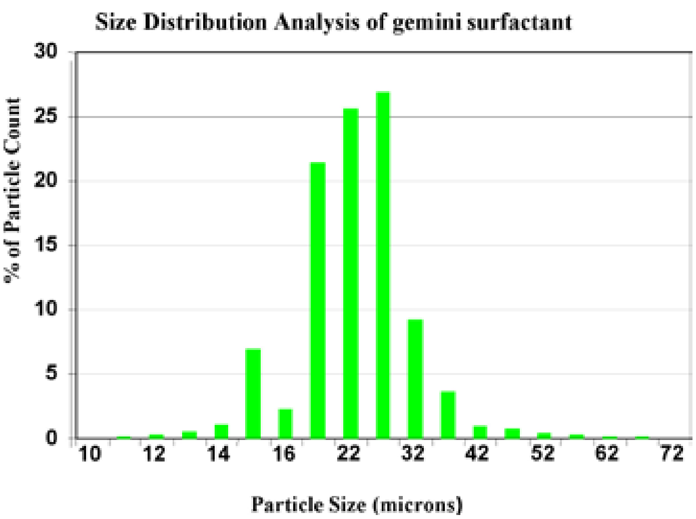

Figure 7 – Particle size of gemini surfactant

Mean size of gemini surfactant found to be 23.64 microns, minimum size of 11 microns and maximum size of 87 microns. This was comparatively having lower species. When the fatliquor was prepared using the gemini surfactant and applied on leather, smaller the species will penetrate better and yields the required performance[36]. From the count chart, it was understood that the spectrum was having narrow Gaussian and required for effective performance. Higher particle size will lead to creaming process, which was determined by the droplet size, difference in the density and viscosity of the surrounding medium. The particle size of the surfactant was small, leading to higher surface area, which resulted the reaction during fatliquoring fast and penetrative. Smaller particles had dominant cohesive and adhesive forces compared to particle weight whereas in bigger particles gravity plays a dominant role. Lesser particle size resulted in increased solubility and performance. Smaller particles and narrower distributions produce better performance than larger particles and broad distributions.

CONCLUSIONS

Conventional surfactant in a fatliquor formulation was replaced by the new gemini surfactant sulfonated gemini malenised soya fatty acid, bridged with butane diol. Reduced dosage of the new gemini surfactant to different extents, applied on wet blue cow leather. Leather properties were studied qualitatively and quantitatively, also through SEM studies. Results were correlated in terms of emulsification power and zeta potential of the surfactants. Surface energies of the fatliquors were calculated and proved the efficiency of the new compound. By the substitution of the gemini surfactant, leather performance can be matched with the reduced dosage to the extent of 66% of which leads to cost reduction and less environmental impact.

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