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Synthesis of fatliquor from waste bovine fat for use in small scale leather industry

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In this study, fatliquor has been synthesized from waste bovine fat for its use in small scale leather industry. The physico-chemical properties of bovine fat are determined before sulphation with sulphuric acid followed by the subsequently neutralization with ammonia to produce the fatliquor. The fatliquor is subjected to chemical and physical analyses. The degree of sulphation is found to be 90% and the surface active groups of the fatliquor are observed in anionic form. The fatliquor has been applied onto light leather and physical tests are carried out on the fixed leathers. The results of the physical tests on fixed leather conform to the standard leather specifications. It is observed that the synthesized fatliquor could be used as an alternative in leather fixation.

Keywords: Bovine fat, Emulsifier, Fatliquor, Leather, Sulphation, Tanning

Leather industries produce large quantities of chromium containing solid and liquid wastes during processing of hides and skins. Disposal of these wastes is expensive and causes environmental pollution. One way of handling leather wastes is to recover useful resources. Research has focused on various methods of managing wastes from the leather processing industry[1-6]. For instance, Taylor *et al.*[7-9] reported the extraction of protein products (gelatin and collagen hydrolysate) from waste leather shavings. Gelatin is used in cosmetics, adhesives, films, printing and photography. Collagen hydrolysate can be used as a fertilizer and animal feed additives. The cake that remains after removal of proteins from leather shavings can be used for purifying chromic oxide. Mu *et al.*[10] reported the enzymatic and alkali hydrolyses of chrome containing leather waste to produce value added leather chemicals. A pilot study on the isolation of potentially valuable proteins from chrome shavings was reported by Cabeza *et al.*[11]. In another research, animal fats obtained from leather fleshy wastes were used to produce methyl esters for biodiesel production[12].

A large quantity of water is eliminated during leather chrome tanning process[13,14]. This process leaves hard intractable leather which is difficult to rehydrate. Lubricants or fatliquors are applied to the leather to keep the fibres apart during drying and to reduce frictional forces within the fibre weave. Proper lubrication or fatliquoring is necessary to obtain leathers with requisite characteristics. This process protects the leather against cracking since it prevents the adhesion of the fibre during drying. The main characteristics of fatliquored leathers are feel, softness, and a certain degree of water repellency. Physical characteristics such as tear resistance, break, and tensile strength, as well as comfort properties of leathers depend on fatliquoring[15]. The fatliquoring process introduces oils and fats into the leather matrix in finely dispersed form. This is attained by emulsification process through introduction of sulphate and sulphonate groups into the structure of oils and fats[16,17] or through addition of surfactants to the composition of fatliquors. Fatliquor emulsions prepared by exposing natural and sulphated fats ultrasonic waves[18-20] have already been reported in literature.

In this study, attempt has been made to evaluate the potential of using fatliquor prepared from waste bovine fat in fixing light leathers. Although the fat content in leather wastes is remarkably high, these wastes are not evaluated effectively and there is almost no application method to recover them. The use of bovine fat to prepare fatliquor is thought to be one solution to waste management. The use of locally synthesized fatliquor as an import substitute ensures a significant cut in import cost. The effectiveness of the prepared fatliquor on fixing light leathers is also compared against the imported fatliquor.

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Experimental Procedure

Separation of fatty matter and non fatty matter

The separation of fatty acid and non fatty matter was done according to a previously reported method[21]. Five gram raw sample was heated under reflux in 10 mL 25% HCl until the bovine fats were clearly separated from the emulsion. The fat was cooled and 50 mL of diethyl ether was added. The acidic aqueous layer was separated from the bovine fat layer using a separating funnel. Residual water in fat mixture was eliminated using anhydrous sodium sulphate followed by filtration. The ether in fat was then distilled off.

Physico-chemical properties of separated bovine fat

Saponification value

The saponification value of fat was determined using the method reported by Gerry and Thomas[22]. Briefly 2.9 g fat was refluxed in 25 mL of 0.5 M KOH for 1 h. The unreacted KOH was titrated with 0.5 M HCl.

Acid value and iodine value

A mixed solvent of benzene (20 mL) and ethanol (40 mL) was prepared. Then 2.0 g of the fat sample was warmed and dissolved in 40 mL of the mixed solvent. The cooled mixture was then titrated with 0.1 M KOH to obtain the acid value.

The iodine value was determined by Wijs method[23]. Iodine trichloride (9.0 g) was dissolved in 1000 mL of glacial acetic acid followed by addition of 300 mL CCl_4 and 700 mL glacial acetic acid. The halogen content was determined by titrating 5 mL of the solution added to 50 mL of 10% aqueous KI solution with 0.1 M sodium thiosulphate. Then 10.0 g of iodine was added before allowing the mixture to stand for 3 days Fat (5.0 g) was dissolved in 5 mL CCl_4 in a stoppered conical flask followed by the addition of 25 mL standardized Wijs solution. The mixture was kept in dark for 30 min at 20°C, and then 50 mL of distilled and 15 mL of 10% KI solutions were added. The liberated iodine was then titrated with 0.1 M sodium thiosulphate.

Synthesis of bovine fatliquor

Fat (500 mL) was placed into an acid resistant vessel with cooling coils through which water was flowing. Then 50 mL of 0.02 M H_2SO_4 was slowly added under continuous stirring. The contents were stirred for 30 min. To prevent loss of combined SO_3, 100 mL of 0.01 M NH_3 was added to the solution to convert the acid sulphate to its alkali salts. Sodium sulphate was removed by washing with brine.

Physico-chemical tests of bovine fatliquor

Temperature and pH stability of emulsion

Ten per cent fatliquor emulsions were prepared by dispersing 5 g of fatliqour in 45 mL of water. The *p*H of the emulsion and percentage phase separations at different temperatures (25-80°C) was determined. Fatliquor emulsion (10%) solutions were then mixed with 5% solutions each of NaCl, $MgSO_4$ and basic $CrSO_4$ in separate containers. The percentage phase separation as a function of time was determined.

Surface active groups

The method of analyzing surface active groups was adopted from Covington[16]. Five per cent (v/v) of fatliqour in distilled water was prepared. To test for cations, two drops of this solution were applied onto a filter paper and one drop of bromophenol solution added to the spot. After one minute, the filter paper was rinsed thrice with distilled water. In anionic test, 1% (v/v) of fatliquor in distilled water was prepared. One millilitre of this solution was added into a boiling tube containing 15 mL of dye and 10 mL of chloroform. The contents were shaken thoroughly. The contents were allowed to stand for 5 min before viewing against transmitted light.

Total organic SO_3

A method developed by Dunken[24] was used in determining total organic SO_3 in fatliqour. Fatliqour (71.0 g) was taken in a 1000 mL volumetric flask, dissolved in water and diluted up to the mark with distilled water. Ten millilitre of the sample solution was transferred into a 250 mL conical flask. Now 15 mL of chloroform and 25 mL methylene blue indicator were added to the conical flask before titrating the mixture with 0.0025 M ammonium chloride.

Application of bovine fatliquor to light leathers

Fatliquor emulsions (10-30%) were prepared in warm (60°C) water and then added to a reactor vessel containing light leathers. The reaction mixture was stirred overnight.

Physico-chemical properties and tests of fixed light leathers

Fat content

Fixed leather specimens were pulverized. Five gram powdered leather specimens were refluxed in 10 mL of 25% HCl until the fat was separated clearly from the emulsion. The fat was cooled and 50 mL of diethyl ether was added. The acidic aqueous layer was separated from the fat layer using a separating funnel. Residual water in the fat mixture was eliminated by anhydrous sodium sulphate followed by filtration. The ether in fat was then distilled off.

Tensile strength and adhesion of finish

Test pieces were cut from fixed leathers. The tensile strength was determined using a tensile tester (SATRA STD 172).

Test pieces were cut from the leather. One centimeter strip of polythene was adhered to one end of the specimen using super glue. The specimen was subjected to finish tester (SATRA STM 432) to determine the strip off weight.

Flexing endurance

Test pieces were cut from the leather and placed on a flexometer (SATRA STD 197). Two ends of the leather specimen were folded and gripped on one end, and then subjected to 20000 flexes, after which any sign of cracking or peeling was observed.

Instant lastometer

A method previously reported by Prester[25] was used to determine instant lastometer of fixed light leathers. Circular leather pieces were cut and placed on instant lastometer tester (SATRA 177) at the bottom circular die. The pump on the recorder was released instantly to exert pressure at the centre of the leather piece. Any cracking sign of the leather was observed.

Rub fastness

Test pieces were cut from the leather. Small damp cotton swabs were placed on a die which was fitted to the rub fastness tester (SATRA STM 421). The leather specimen was gripped on the lower platform and subjected to 300 wet rubs. The specimens were subjected to the rub fastness test before and after aging.

Results and Discussion

Table 1 shows the physico-chemical properties of bovine fat. A remarkably high percentage (>90%) of fatty matter clearly indicates that the bovine fat contains sufficiently large amounts of fats that can be chemically modified for synthesis of fatliquors. A low iodine number shows that the fat has a low quantity of unsaturated fatty acid[26]. Since high degree of saturation leads to insignificant oxidation, this bovine fat can be used in fatliquoring. A low iodine number also indicates a high melting point and soft lubricating value of the bovine fat. The iodine value is used to determine the degree of unsaturation of the fatty acids. It is found that oleic acid is the main fatty acid present in bovine fat[19]. A high acid value observed shows that the bovine fat is rancid and contains many free fatty acids. The most probable identities of the saturated fatty acids in bovine fat are palmittic[24,27] and stearic acids.

The physico-chemical properties of bovine fatliqour are shown in Table 2. A translucent emulsion is indicative of a high degree of sulphation. This physical observation confirms that there is a high percentage of SO_3 incorporated in the organic matrix. A translucent emulsion is aresult of the inability of oil globules to scatter light. Milky emulsions are indicative of low degree of oil sulphation. The combined SO_3 or emulsifier is the fuel which drives the oil droplets into the leather. Anionic emulsifiers ensure a great degree of fixation since they will be attracted to the positively charged leather surface. Surface active anionic substances (sulphates and carboxylic) and cationic moieties namely amines groups and amine salts are chemically detected in the fatliquor. The existence of oppositely charged moieties ensures strong electrostatic forces of attraction within fatliquor molecules[28].

Table 3 shows the effect of increasing temperature on the stability of the fatliquor emulsion. The emulsion remains stable up to 65ºC. Above 65ºC there

Table 1— Physico-chemical characteristics of bovine fat

Characteristic	Mean value*
Fatty matter, %	90.0 ± 0.4
Iodine value, g of I_2/100 g oil	50.3 ± 0.8
Saponification number, mg KOH/g	195.7 ± 0.6
Melting point, °C	24.2 ± 0.2
Acid value	132 ± 0.7
Unsaturated fatty acid, %	14.0 ± 1.3
Free fatty acids, %	93.0 ± 0.5

*Mean ± SD triplicate analysis.

Table 2— Physico-chemical characteristics of bovine fat

Characteristic	Value
Stability, months	48
*p*H of emulsifier	12.5 ± 0.1*
*p*H of leather	10.5 ± 0.2*
Surface active groups	Anionic
Total organic SO_3, %	90 ± 0.4*
Appearance	Translucent

*Mean ± SD triplicate analysis.

Table 3— *p*H and temperature stability of fatliqour emulsions

Temperature, ºC	*p*H	% water separation
25	7.1	1.4
30	7.2	3.5
35	6.9	4.3
40	7.2	5.1
45	7.1	6.2
50	6.8	7.1
55	6.9	9.4
60	7.3	11.2
65	7.2	13.3
70	7.3	40.2
80	7.0	50.1

is a substantial increase in phase separation (13% at 65ºC to 40% at 70ºC). Jones *et al.*[29] proposed that an increase in temperature reduces the viscosity of oil and increases the mobility and settling rate of water droplets. An increase in temperature also increases the frequency of drop collision and favors coalescence. An elevated temperature breaks the interfacial film on droplets because of water expansion and enhances interfacial film drainage and coalescence. The differences in densities of water and oil increases with increase in temperature further enhancing water-settling time. The *p*H of the 10% fatliquor emulsion is found to be between 6.8 and 7.4. This *p*H range is very much close to the optimum *p*H specifications (6.5-7.5) of sulphated fatliquors used for lubrication of leathers[30]

Inorganic salts affect the stability of emulsions (Fig. 1). The emulsion is stable for at least 40 min (less than 20% phase separation) in all the three salts. However, after 40 min, higher divalent ions and high *p*H enhance destabilization of the emulsion as indicated by a higher phase separation in aqueous $MgSO_4$ and basic $CrSO_4$ than in NaCl. The divalent ions chemically react with hydrophilic groups to form insoluble salts. Such chemical interactions destroy the interfacial film resulting in oil and water separation[31,32].

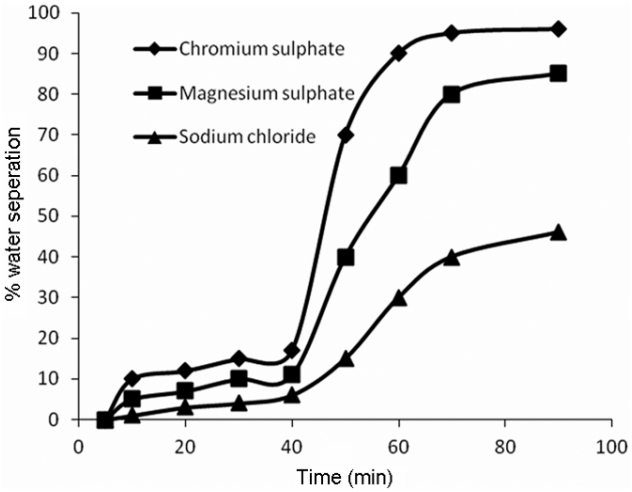

Fig. 1— Effect of ionic salts on stability of 10% fatliquor emulsion

Figure 2 shows the variation of fat fixed per unit weight of light leather as a function of percentage of fatliquor. A high percentage (>70%) is fixed upon application of 15-30% fatliquor per unit weight of light leather. A high fixed fat content indicates that the electrostatic attraction between oil and leather stabilizes the bond upon drying. Despite high percentages of oil fixation at 30% fatliquor per unit leather weight, the leather shows heavy and low collagen density areas. Lining shows the highest percentage of fixed fat content because it is the lightest of all leather types. Lining has a small cross-section (thickness 0.8-1.0 mm), enabling greatest oil penetration. Upholstery, renaissance and saco leathers show similar fixed fat content because they have same thickness (1.1-1.2 mm). The minor differences in fixed fat content can be attributed to variations in the way these leathers are processed depending on their application. Ecoline has the least percentage of fixed leather because it is the thickest leather (1.4-1.5 mm).

Physical tests of different light leathers are shown in Table 4. Adhesion of finish is an important test since it determines the final appearance and sale ability of the leather. Values of adhesion of finish are

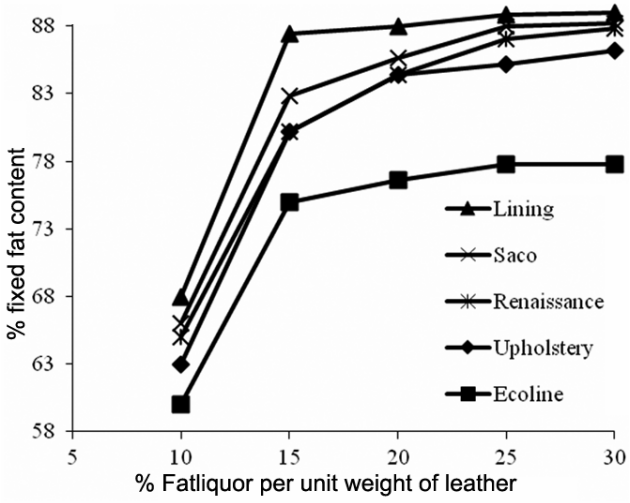

Fig. 2— Percentage fixed fat content as a function of quantity of fatliquor applied per unit weight of different light leathers

Table 4— Physical tests of different light leathers

Physical test	Leather type					Specification
	Renaissance	Lining	Saco	Ecoline	Upholstery	
Instant lastometer (at 7 mm)	N	N cracking	N	N	N	N cracking
Flexing, flexes	N	N	N	20 000	N	20 000
Adhesion of finish, Ncm^{-1}	4.7	5.2	8.1	7.8	6.9	2.5 (min)
Rub fastness, cycles	300	N	N	N	300	300
Tensile strength, N/mm	140	60	145	152	136	50

N–Physical test inappropriate for the leather type.

all above the specifications indicating that the fatliquoring is effective. Rub fastness tests are specifically done on renaissance and upholstery leathers that are used in furniture industry. This test is performed to determine whether the finish will remain attached to these leathers over long period of time. The leather does not peel off after ageing confirming good adherence of the finish. There is no clearly defined trend on adhesion of finish values. This can be attributed to the fact that this physical parameter is affected by other factors such as lacquers waxes making up the finish, the type and conditions applied during plating. Ecoline leather (used for shoe uppers) does not show any signs of peeling off after 20000 flexes showing the effectiveness of the fatliquor. The lining leather shows no cracking upon subjecting it to instant lastometer test. Values for tensile strength are well above specifications (50 N/mm) for all leather types. Ecoline has the highest tensile strength because it is the thickest leather. Lining, the thinnest leather has the least tensile strength.

Conclusion

Bovine fatliquor has demonstrated its potential to be used in fixing light leathers. The physico-chemical properties of the bovine fat, emulsion stabilities and quality of the leather have shown that the fat extracted from bovine waste during the tanning process is a potential raw material for producing fat liquors in leather industry. This economically feasible process of utilizating leather waste provides an effective way of solving waste disposal problems.

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