Synthesis of Biological Based Anionic Fatliquor and Its Application on Leather

by

M. K. Pervez,* F. Ahmed, S. J. Mahboob, R. Dewani, H. R. Nawaz, M. Zeeshan and T. Ayaz

Leather Research Center, D/102, S. I. T. E., South Avenue, Pakistan Council of Scientific and Industrial Research,
Karachi-75700, Pakistan

Abstract

In this study, three types of anionic fat-liquors are prepared from various vegetable oils by sulfation process. One fat-liquor is made from pure canola oil, the second one from castor oil and the third one is made from a mixture of different oils, which is termed here as 'Blended oil'. Canola oil is used for fat-liquoring purpose and has been compared with other natural oil based fat-liquors and a commercially available sulfated fat-liquor. Different chemical and physical studies were carried out to find out the fat-liquor producing the best results. Chemical studies of fat-liquor such as pH, fat content, solid content, moisture and organically combined sulfuric anhydride were determined before its application on leather. The physical studies such as tear strength, tensile strength, elongation, burst load, softness and distention were carried out on crust leather. The fat content test was carried out to check the uptake of fat-liquors by leather samples. On the basis of chemical and physical analysis the blended oil based fat-liquor was found to be better than the castor & canola oil based fat-liquors and commercially available sulfated fat-liquor.

Introduction

The history of leather is as old as the history of mankind and leather has been used in different forms according to its types and shapes (articles). Skin or hide is converted into useful leather article after different chemical and mechanical processes and fatliquoring is one of the key stages in leather processing. The natural fats from the skin are removed in the beam house operations and the leather becomes stiff and loses its physical properties. Therefore, modified oil is introduced into the leather matrix in the form of fat-liquor (in aqueous medium) through fat-liquoring process, which creates an emulsion. The emulsification is achieved by sulfation, sulfonation and sulfitation processes. Three different types of functionalities are introduced which modify the oil with three different types of functional groups such as sulfate, sulfonate and sulfite. Different types of fat-liquors have been used widely in fat-liquoring process to remove the stiffness of leather and make it soft and strong.

The tanners use sulfated fat-liquor for maximum take up on chrome tanned leather, while take up is difficult on vegetable tanned leather and in case of alum tannage the emulsion simply breaks out.[1] Sulfated fat-liquor is generally used for the production of split, grain and chrome tanned leather, especially lining, shoe upper and garment leather. Fat-liquor gives softness, flexibility, dispersion and warm handle to the leather and also improves the mechanical properties of leather. Some fat-liquors have biological origin, such as vegetable oil, fats, animal fats, oils and waxes (both from vegetable and animal sources), while others are obtained from non-biological sources such as mineral oils, fatty alcohols and processed hydrocarbons etc.

There is always a need for a good vegetable oil based fat-liquor in leather industry, due to its biodegradability and desired leather properties such as tear strength, tensile strength, break and comfort of leather. Palop *et al.*[2] synthesized sulfited fat liquors and studied their properties: softness, thickness, tensile strength, tear load, fat content etc., and concluded their results on the basis of comparative studies among three different sulfited fat liquors. M. Gutterres *et al.*,[3] used different methods of analysis to study the chemical and physical properties of leather. The sulfation of castor oil with concentrated sulfuric acid had already been started in early 1970s at high temperature and with long reaction times.[4,5] M. H. Cuq *et al.* reported the characteristics of the extracted fatty substances from seal skins and they used the extracted fats as fat-liquors in leather manufacturing.[6] B. C. Nyamunda *et al.* synthesized fat-liquor from waste bovine for small scale leather industry and they used it as an alternative in leather fixation.[7]

In this study, three different types of anionic fat-liquors were synthesized from various vegetable oils, their chemical properties were studied and the fat-liquored leathers were evaluated on the basis of their physical properties. The chemical and physical properties were also compared with those of the commercially available fat-liquor, used as a reference material in this study.

*Corresponding author e-mail: dr.kpervez@gmail.com; Tel: +92 300 2294131
Manuscript received February 22, 2015, accepted for publication April 30, 2015.

EXPERIMENTAL

The fat-liquors were prepared by sulfation process using concentrated sulfuric acid and neutralized by basic solution. The anionic sulfated fat-liquor used as commercial reference material is 'Derminol CST Liquid,' purchased from local market and applied to leather.

Sulfation

Canola oil (1 kg) was contained in a jacketed steel sulfonator (see reactor diagram in Figure 1) and 25-30% concentrated H_2SO_4 (by weight of oil) was added drop-wise with the help of a dropping funnel, in one hour at 15-20 °C (controlled temperature). Addition of acid to oil is exothermic so the temperature was controlled by cold water circulation through the jacket of the sulfonator and adequate mixing of the reactants with a central agitator (see Figure 1). The emulsifying ability of the modified oil with water was checked real time (one or two drops of the sulfated oil in water forming white colored liquid). After acid addition, the mixture was stirred for another 4 hours and left overnight for the reaction to complete at room temperature (25-30 °C). The sulfated oil was washed with brine solution and basified with sodium hydroxide solution (10%) to bring the pH in between 6.5-7.0.

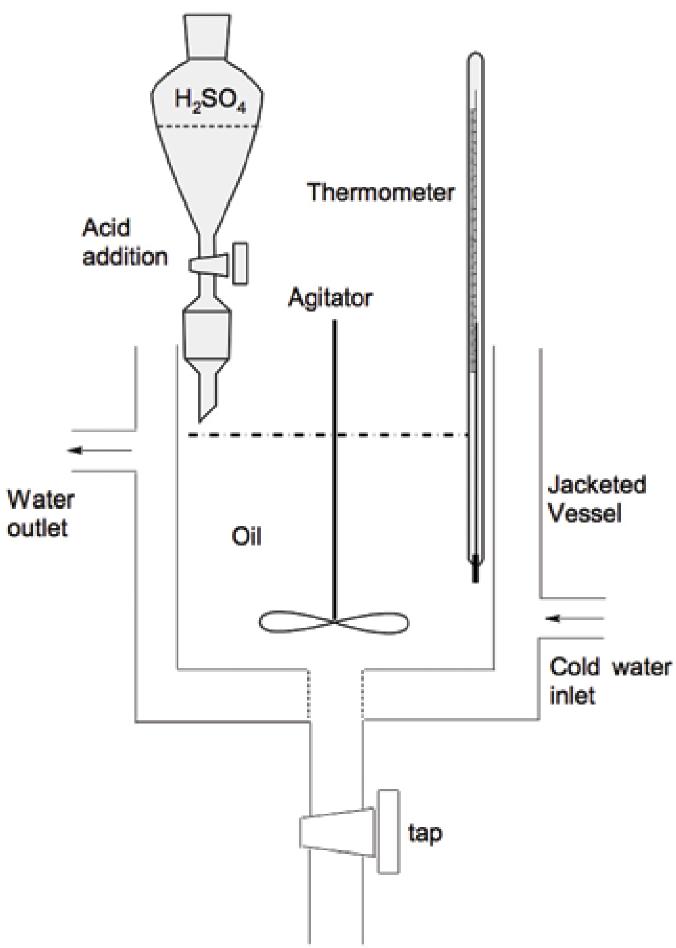

Figure 1. Sulfonator (Jacketed steel reactor.)

The blended sulfated oil was a mixture of four oils namely; cotton seed, mustard, coconut and castor oil. Initially, the blend of three oils, cottonseed (1.5 kg), mustard (1 kg) and coconut (1/2 kg) were sulfated while castor oil (1 kg) was sulfated separately. The mixture of three oils (cotton seed, mustard and coconut) and castor oil were mixed in a ratio of 40:60 respectively. The rest of the steps are the same as carried out in the case of canola oil. After synthesis, the chemical and physical testing of all three types of fat-liquors from canola, castor and blended oil was performed and the results were compared with that of the commercially available fat-liquor. The fat-liquors were applied on sheep leather and the leather samples were evaluated through different physical and chemical tests. The choice of sheep leather is justified by the fact that the evaluation and comparison of fat-liquors is based on the strength, softness and quality that they confer to leather and sheep leather has the capability to be made extremely soft.

Fat-liquoring

The sheepskin was converted into wet blue through all the necessary steps of leather processing. The wet blue was shaved to 1.0 mm thickness. The trials were carried out in experimental plastic drums measuring 60 cm in diameter and 30 cm in width respectively. The fat content of wet blue was determined at this stage to estimate the natural fat present in the leather. The tanned leather or wet blue was washed with 200% tap water. The leather was neutralized until the pH was raised to a range of 7.0-7.5, by the addition of 0.75% sodium bicarbonate and sodium formate, each on the weight of wet blue. The neutralized leather was washed with 400-500% tap water. The leather was retanned with commercial syntans and polymers. The whole tanned sheep leather was divided into four parts. The semi-processed leather pieces were fat-liquored with 10% (on the weight of leather) laboratory synthesized and commercial fat-liquors separately. All fat-liquors were applied singly and not in any combination with other fat-liquors. During fat-liquoring the temperature was kept in between 50-60 °C. Finally, the fat-liquors were fixed with 1% formic acid solution. The leathers were washed with plain water, piled and hang dried. After drying, the leathers were ready for different chemical and physical tests. All the chemical and physical tests were performed in triplicate and the mean value is reported.

Chemical Testing of Fat-liquors

The pH of all four fat-liquors was measured using a JENWAY 3510 pH meter. The calibration was performed with pH 4.0, pH 7.0 and pH 10.0 buffer solutions from Scharlau. The determination of pH (see Table I and Figure 2) was carried out according to the SLTC test method SLC-308.[8] The fat content, solid content, moisture content and the combined sulfuric anhydride percentage in all fat-liquors were determined according to the SLTC and ASTM standard test methods SLC-319,[9] D 4906-95,[10] SLC-307[11] and D 5351-93[12] (see Table I and Figure 3) respectively. The fat content of all fat-liquored leathers was determined according to the SLTC test method SLC-4[13] (see Table III).

Physical Testing of Fat-liquored Leather

Physical tests such as tear strength, tensile strength, elongation at break, burst load, distention and softness were performed according to the standard SLTC test methods IUP-8,[14] IUP-6,[15] SLP-9[16] and IUP-36[17] respectively. Tensile & Tear Strength, Elongation, Bursting & Distension were performed on a Single Column Bench top Tester *Tinius Olsen*-H5KS. The softness test was performed on ST-300 Softness Tester. All physical tests were performed after the application of various fat-liquors on sheep leather (see Table III and Figure 4 for test results).

RESULTS AND DISCUSSION

Pure, blended and commercial (Derminol CST Liquid) anionic fat-liquors were applied on sheep leather. The various chemical and physical tests were performed according to the standard test methods and results were studied and evaluated.

Chemical Analysis of Fat-liquor

The chemical properties of the commercial fat-liquor as declared by the manufacturer are as follows (see table II):

All the fat-liquors appeared as clear dark brown oils. The pH of the fat-liquors based on canola, castor and blended oils in 10% solution is 5.35, 6.50 and 6.37 respectively (see Table I and Figure 2). The pH of the commercial fat-liquor is 6.38, nearly same as that of blended oil based fat-liquor. All studied fat-liquors are anionic in nature having pH values slightly on the acidic side that is below 7. The pH of the canola oil based fat-liquor is lower as compared to the castor and blended liquors which are better for chromed tanned leather because the emulsion is stable at lower pH and emulsion stability is crucial for the fat-liquoring process.[18] The low pH of canola oil is helpful as an emulsifier for better penetration into leather fibers to remove stiffness. The pH of canola based fat-liquor is more acidic as compared to the other three fat-liquors, which are just slightly acidic in nature (see Table I and Figure 2), but the water emulsions of all fat-liquors are milkier than former.

The fat contents of different fat-liquors are in the range 71-85% and the results show that there is no big difference between the fat contents of the four fat-liquors (see Table I and Figure 3). The solid content of blended vegetable oil based fat-liquor is 93.52% which is higher as compared to castor and canola oil based fat-liquors and commercial fat-liquor i.e. 88.5%, 84.25% and 88.0% respectively, hence the solid contents do not affect the quality of leather. The moisture value of canola oil based fat-liquor i.e. 15.7% is higher than the castor and blended oil based fat-liquors and also commercial

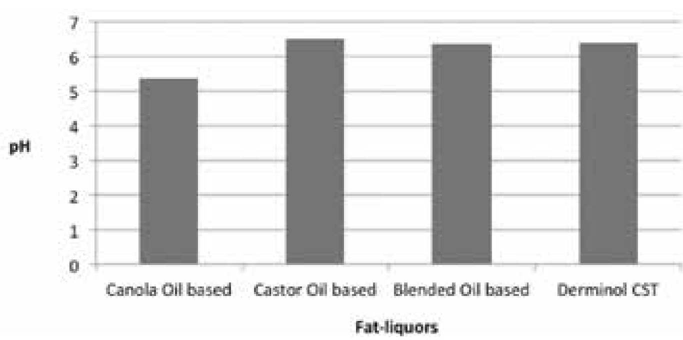

Figure 2. Comparison of pH values of different synthetic fat-liquors.

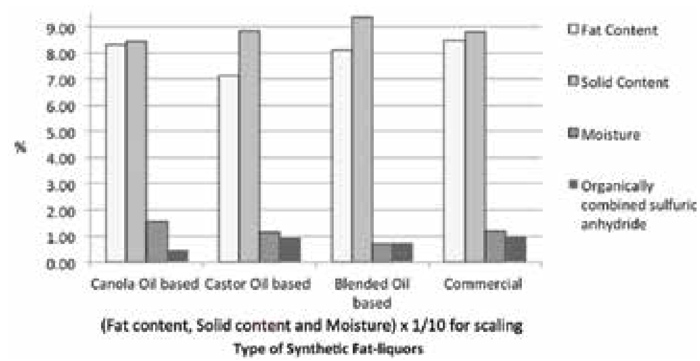

Figure 3. Comparison of fat, solid, moisture content and organically combined sulfuric anhydride of fat-liquors.

TABLE I
Chemical properties of fat-liquors.

Fat-liquor based on	pH k=2	Fat Content (%)	Solid Content (%)	Moisture (%)	Organically combined sulfuric anhydride (%)
Canola oil	5.35 ± 0.03	83.0 ± 0.10	84.3 ± 0.5	15.7 ± 0.50	0.45 ± 0.01
Castor oil	6.50 ± 0.03	71.5 ± 0.10	88.5 ± 0.4	11.5 ± 0.40	0.93 ± 0.02
Blended oil	6.37 ± 0.03	81.0 ± 0.20	93.5 ± 0.2	6.8 ± 0.20	0.72 ± 0.01
Commercial Fat-liquor	6.38 ± 0.03	84.7 ± 0.17	88.0 ± 0.2	12.0 ± 0.20	1.00 ± 0.01

fat-liquor which are 11.5%, 6.8% and 12.0% respectively (see Table I and Figure 3). Actually, at the time of fat-liquoring the leather uptake of the canola oil based fat-liquor is lesser as compared to blended because the moisture is already present in the canola which affects the quantity of fat-liquor take up at the time of fat-liquoring. The percentages of combined sulfuric anhydride are 0.45%, 0.93%, 0.72% and 1.00% for canola, castor and blended oil based fat-liquors and commercial fat-liquor respectively (see Table I and Figure 3). The percentage of organically combined sulfuric anhydride value of castor oil based fat-liquor revealed that the sulfuric acid chemically combined with the different carbon chain units in castor oil in a higher ratio as compared to canola and blended oil based fat-liquors. The percentage of organically combined sulfuric anhydride value of commercial fat-liquor is approximately the same as castor oil based fat-liquor. The fat content or percentage of extractable fats & oils after fat-liquoring shows the quality of leather. The percentage of fat content in wet blue sheep leather was determined to be 1.51 ± 0.03 (On moisture free basis).

The percentage of fat content of canola, castor and blended oil based fat-liquors are approximately the same but the commercial fat-liquor when applied on leather shows higher fat content in leather as compared to canola, castor and blended oil fat-liquors. In comparison of the vegetable oil based fat-liquor, the fat content results show that the leather absorbed more quantity of blended oil (see Table III). In case of commercial fat-liquor (Derminol CST Liquid), the percentage of fat content is much higher than the other fat-liquors (see Table III and Figure 4).

The quality of leather fat-liquored by commercial fat-liquor is not as good as compared to the leather processed with natural

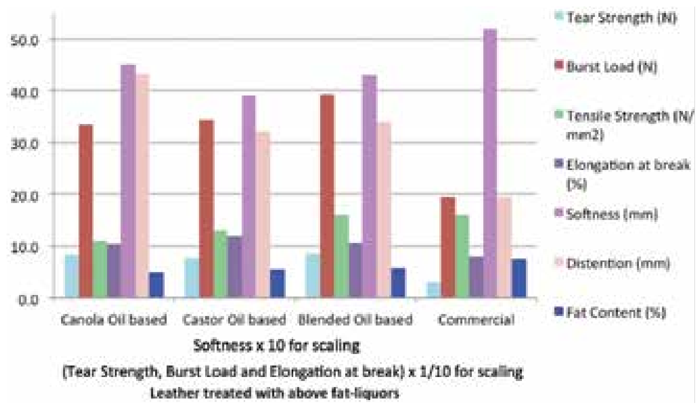

Figure 4. Comparison of physical and chemical properties of fat-liquored leather.

TABLE II
Chemical properties of commercial fat-liquor (used as reference.)

Commercial Sulfated Fat-liquor	pH	Active substance (%)	Ionic Character	Chemical Character
Derminol CST Liquid	6.0-7.5	min. 78	Anionic	Sulfated natural & synthetic oil

TABLE III
Physical and chemical properties of leather.

Leather processed with Fat-liquor based on	Tear Strength N (k=2)	Tensile Strength N/mm^2 (k=2)	Elongation at break % (k=2)	Softness mm (k=2)	Burst Load N (k=2)	Distention mm (k=2)	Fat Content (%) k=2
Canola oil	83.7 ± 7.1	11.0 ± 0.33	104.4 ± 0.78	4.5 ± 0.02	333.3 ± 4.71	43.2 ± 3.48	4.85 ± 0.07
Castor oil	78.6 ± 4.4	13.1 ± 1.48	120.6 ± 1.98	3.9 ± 0.01	343.8 ± 5.52	32.3 ± 2.05	5.63 ± 0.08
Blended oil	86.1 ± 4.9	16.0 ± 2.5	105.1 ± 0.76	4.3 ± 0.02	392.6 ± 3.53	34.0 ± 4.79	5.81 ± 0.08
Commercial Fat-Liquor	31.9 ± 2.16	16.1 ± 1.22	79.6 ± 3.64	5.2 ± 0.03	195.6 ± 6.12	19.4 ± 0.63	7.61 ± 0.12

oil based fat-liquor. It is the evident that the commercial fat-liquor penetrates easily into the leather as compared to other fat-liquors but it does not add to other physical properties of leather except softness (see Table III and Figure 4). On the basis of chemical results, it is evident that the blended oil fat-liquor has better chemical properties and gives good results on leather.

Physical Analysis of Fat-liquored Leather

Physical properties show the strength and softness of leather. In this research the tear strength, tensile strength, elongation, burst load, distention and softness have been studied. The test results of physical properties are given in Table III and Figure 4.

The graphical representation shows the fat-liquor that gives good strength and softness to the leather. The blended oil based fat-liquor shows greater tear and tensile strength as compared to the canola, castor oil and commercial fat-liquors. The minimum requirement of tear strength for shoe upper leather are 35 N for lined shoe, 50 N for unlined shoe and 100 N for children and safety shoes.[19] On comparison, it is clear that the synthesized fat-liquors have produced leather with tear strength values suitable for shoe upper leather, while the values provided by commercial fat-liquors are way too low. Similarly the minimum requirement of tensile strength (elongation at break) for shoe upper leather is 40%, and almost all the leather samples show a tensile strength higher than this benchmark (see Table III and Figure 4). For sheep leather, the minimum acceptable value (strength at break) comes out to be 12 N/mm^2 and as mentioned earlier, all the tensile strength values are comparably higher and suitable for shoe upper leather but because of very low tear strength, the commercial fat-liquor is not fit for the manufacturing of shoe upper leather.[19, 20]

Generally, the minimum requirement of tear strength for shoe lining leather is 15 N and if the lining has a strengthening function then the value goes to 30 N. Canola, castor and blended oil fat-liquored leathers supersede this value by a greater margin and are most suitable for making shoe lining leather (see Table III and Figure 4), whereas commercial fat-liquored leather merely passes the test (30 N).[19, 20]

Similarly, the minimum requirement of tear strength for upholstery leather is 50 N.[19] According to the test results, the tear strengths of canola, castor and blended fat-liquored leather clearly exceed this value but the commercial fat-liquored leather does not and it does not produce leather strong enough for upholstery (see Table III and Figure 4).

The minimum tear strength for garment leather is 30 N[19] and all fat-liquored leathers have tear strengths suitable for making garment leather (see Table III and Figure 4). Canola, castor and blended fat-liquored leather are comparatively more suitable for garment leather as compared to the commercial fat-liquored leather, especially in the cases where softness is not the prime requisite (see Table III and Figure 4).

The minimum tensile strengths required are 20 N/mm^2 (2000 N/cm^2) and 22.5 N/mm^2 (2250 N/cm^2) for insole and sole leathers respectively.[19, 20] According to the test results (see Table III and Figure 4) all fat-liquored leathers lag behind on these criteria and they are not fit for either insole or sole leather.

Softness property of the commercial fat-liquor is comparatively superior to that conferred by other fat-liquors. The blended oil based fat-liquor gives nearly the same softness to leather as the canola oil based fat-liquor, but is higher than castor oil based fat-liquor. The softness results also correspond to the higher uptake of commercial fat-liquor in leather. Apart from the experimental results the soft touch and handle of all the four fat-liquored leathers is almost the same. The value of burst load is another factor, which represents the strength of leather after fat-liquoring (see Table III and Figure 4). The overall physical performance values of the leather treated with commercial fat-liquor are not as good as compared with the other fat-liquors except softness.

Conclusion

In the current study, five different oils were used from vegetable sources to synthesize fat-liquors having biological and natural origin for the protection of environment. From these five vegetable oils, three different anionic fat-liquors were prepared, and their chemical and physical properties were studied and compared with the commercially available sulfated fat-liquor, used as a bench mark. On the basis of the various chemical tests, the fat-liquor based on blended oil is found to have better fat-liquoring properties as compared to the fat-liquors based on castor oil, canola oil and commercial fat-liquor. But this does not imply that Derminol CST Liquid and the fat-liquors based on castor oil and canola oil do not have the capability to produce good leather, in fact it is superior especially for garment leather. The castor oil based fat-liquor is already being used widely in tanneries as leather auxiliary by the commercial name of Turkey Red Oil (TRO), having good fat-liquoring property, while canola oil based fat-liquor is also a good fat-liquor but not comparable with those based on blended and castor oil. It is also worth to mention here that the leather prepared with canola oil based fat-liquor was comparatively glossier than the other three. This also reflects in the result of fat content which is higher in canola oil based fat-liquor as compared to others. The blended liquor also has excellent fat-liquoring property but it is expensive as compared to castor and canola oil based fat-liquor. Canola oil based fat-liquor is low cost and has all the important physical and chemical properties desirable for a good fat-liquor. Apart from commercial fat-liquored leather, canola, castor and blended oil fat-liquored leather are found suitable for the manufacturing of shoe upper, shoe lining and upholstery leathers. All fat-liquors are suitable for making garment leather whereas they do not produce good quality sole and insole leathers. Finally the blended fat-liquor bears excellent quality and produced good quality leather among all the fat-liquors studied.

ACKNOWLEDGEMENTS

We are thankful to the Tannery and Leather Technological Division (LTD) of Leather Research Centre (LRC) and appreciate their technical support and co-ordination for this research work. We are also thankful to Mr. Fazil, Mr. Sartaj and Mr. Shakeel of Chemical Research Division (CRD) for their co-operation in this study.

REFERENCES

1. O'Flaherty, F. and Roddy, W. T.; The Chemistry and Technology of leather, Process Control of Leather Quality, Reinhold Publishing, New York, Vol. 3, 61-72, 1978.
2. Palop, R.; Fat-liquoring Influence in Leather Physical–Chemical Properties. XVI Latin American Leather Technicians and Chemists' Congress. Buenos Aires, 2004.
3. Gutterres, M. and Santos, L. M. D.; Study of Fat-liquoring Parameters Using Experimental design, *J. Soc. Leather Tech. Chem.* **93**, 171-175, 2009.
4. L. Kai; Proceedings of the 2009 International Conference on; Chemical, Biological and Environmental Engineering (CBEE 2009), World Scientific Publishing Company Pte. Ltd. 315-322, 2010.
5. Kremers, F. J.; "The sulfonation of castor oil with sulfur trioxide", *J. Am. Oil Chem. Soc.,* **48**(7), 314-317, 1971.
6. Cuq, M. H., Benjelloun-Mlaya, B., and Delmas, M.; Oil Extracted from Seal Hides: Characterization and Use as Leather Fat Liquor, *J. Am. Oil Chem. Soc.***75** (8), 1015-1019, 1998.
7. Nyamunda, B. C., Moyo, M., and Chigondo, F.; Synthesis of fat-liquor from waste bovine fat for use in small scale leather industry, *Indian Journal of Chemical Technology* **20**, 116-120, 2013.
8. Official Methods of Analysis, SLC-308 "Determination of pH of Sulphated Oils", *The Society of Leather Technologists and Chemists,* 220, 1996.
9. Official Methods of Analysis, SLC-319 "Determination of Total Fat in Sulphated Oils", *The Society of Leather Technologists and Chemists*, 234-235, 1996.
10. ASTM D 4906-95 "Total Solids and Ash Content in Leather Finishing Materials", ASTM International. Annual book of ASTM standards 2005. Vol. 15.04, 490-491, 2005.
11. Official Methods of Analysis, SLC-307 "Determination of Water", *The Society of Leather Technologists and Chemists*, 219, 1996.
12. ASTM D 5351-93 "Determination of Organically Combined Sulfuric Anhydride by Extraction Titration", ASTM International. Annual book of ASTM standards 2005. Vol. 15.04, 538-539, 2005.
13. Official Methods of Analysis, SLC-4 "Determination of Substances (Fats and other Solubles) Soluble in Dichloromethane", *The Society of Leather Technologists and Chemists*, 111-113, 1996.
14. Official Methods of Analysis, IUP-8 (SLP-7) "Measurement of Tear Load-Double Edge Tear", *The Society of Leather Technologists and Chemists,* 418-420, 2001.
15. Official Methods of Analysis, IUP-6 (SLP-6) "Measurement of Tensile Strength and Percentage Elongation", *The Society of Leather Technologists and Chemists,* 411-414, 2001.
16. Official Methods of Analysis, SLP-9 "Measurement of Distension and Strength of Grain by the Ball Burst Test", *The Society of Leather Technologists and Chemists*, 281-283, 1996.
17. Official Methods of Analysis, IUP-36 (SLP-37) "Measurement of Leather Softness", *The Society of Leather Technologists and Chemists*, 458-460, 2001.
18. Thorstensen, T. C.; Practical Leather Technology, Krieger Publishing Company, Florida, 4th ed., 202-221, 1993.
19. Luijten., J. A. J.; Physical and Fastness Testing of Leather. Textbook for the Course Leather Quality Control. TNO Centre for Leather and Shoe Research, 2nd September-29th November 1991.
20. Ashebre1, M.; Performance of Leather Uppers of Local Footwear Products and the Determinants, *IJOART* **3** (3), 26-30, 2014.