

# **Egyptian Journal of Chemistry**

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# Leather Fatliquoring Agent from Camel Hump Fat

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## Abstract

In this work, a trial to use camel humps fat to formulate leather fatliquor has been achieved. The hump fat has been chemically treated via sulfition process using sodium metabisulfite, sulfited fat has been neutralized, extracted by salting out technique and subjected to chemical evaluation. The stability of fatliquor emulsions (10 % w/w: sulfited fat to water) has been investigated towards different factors incorporated into leather manufacture such as metallic ion, tanning agents, and pH. The fatliquor shows great stability against different factors. The fat droplets of the fatliquor emulsion were able to penetrate the leather fiber reaching fibrils and adding the required fatty material to the treated leather causing the desired flexibility and softness. A significant enhancement in mechanical properties (tensile strength and elongation at breaks) has been recognized, the morphology study of the fatliquored leather fibers using SEM shows that the leather fiber has been coated with a thin film of fat. The work success to formulate of value product agent from a local abundant natural resource.

Keywords: Hide and skin - leather - fatliquoring - natural resources- hump fat - leather fibers

# 1. Introduction

Natural leather is the oldest natural material used by humans as a natural fiber or polymer. Transferring animal hide or skin into leather involves using a lot of chemicals through complicated steps. The tanning process includes fixing skin protein chains. During beam house, the protein layer which represents the real skin substance is separated by taking away the flesh and the fat to promote the crosslinked between protein and tanning agent. Tanning agents connect the protein function groups [-OH, -COOH, -HN2, -NH-] through a multi-link of the collagen [1].

The chains protein fixation keeps the tanned leather harsh, inflexible, and unusable, Therefore, it has to restore its flexibility. It should treat with fat emulsion to over gain the fat between leather fiber. Therefore, the tanned leather has to be subjected to fatliquoring process. The process involves introducing fat into hard tanned leather [1]. The fat is applied as fat in water emulsion. Accordingly, the fat has to be chemically treated to create a hydrophilic head and the fat can be emulsified into the water phase. Building the fatliquor emulsion is a very sensitive process, therefore, the fat droplets have to possess the ability to penetrate the fibers and coat fibrils promoting sliding of the fiber bundles. The accumulation of the fat on the surface creates a greasy feel and should be prevented. [2]. Fatliquor should exhibit light color and soft leather with soft-smooth texture to offer the consumer's demands. In primitive tanneries, crude oils were used without chemical treatment based on their higher iodine value. The unsaturated bonds permit the oils to attach to the collagen. However, crude oils do not produce the desired fatliqure properties. Fish oil, cod liver oil, neat foot oil were the traditional oils used in this regard [3]. Regarding the shortage of natural resources, researchers are devoted to finding suitable fatty matters to be treated and utilized as leather fatliquors or other industrial applications [4]. The fatliquor emulsion has to be stable up on fatliquoring time in order to exhibits the desired liquoring effect and the micro size droplets can reach the fiber. Therefore, the emulsion should be stable even in the presence of dying materials, metallic ions in addition to the pH variation [5]. Even though natural oils are renewable materials, they are not available in abundance due to competition with human food needs and pricey costly. Mineral resources have been developed in this regard, but they have negative environmental challenges in addition to the high price and non-renewability. The camels are desert animals that are abundant in the tropics. They are characterized

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**Receive Date:** 04 February 2022, **Revise Date:** 05 March 2022, **Accept Date:** 21 May 2022, **First Publish Date:** 21 May 2022 DOI: 10.21608/EJCHEM.2022.120134.5391

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by the presence of large humps that store a large amount of fat. Hump fats are a by-product of camel meat production in slaughterhouses. The large quantities of hump fat that are available in local slaughterhouses make these fats a promise bio-sources that can be processed to obtain value-added products. Mirgani studied the major fatty acids composition of hump fat. According to the author, the major components of the fatty acids is 35 % palmitate, 26 % stearate 24 % oleate and 12 % myristate, and hexadecenoic and pentadecanoic acids were minor components 2% [6]. Therefore, this fat can be utilized as an oleo-chemical resource. Sbihi et al studied the physio-chemical properties of the hump fat [7], according to the study, it was found that the saponification value is 202.3KOH/g oil and the iodine value of Hachi fat (small camels) is 62.74 g/100 g oil, and the fat was composed primarily of oleic acid (33.35%), followed by palmitic acid (26.16%), stearic acid (10.07%), palmitelaidic acid (9.56%) and myristic acid (8.83%). Therefore, the higher iodine value and higher saponification value of the fat encourage the usage of the fat as an oleochemical resource. According to the study, Hachi fat could be used as an important source of biological materials. The fat can be chemically modified to introduce hydrophilic heads depending on its considerable degree of unsaturation, in this work a trial to modify the hump fat via sulfition process to formulate leather fatliquoring agent has been achieved, the work is a trial to utilize the hump fat as an oleochemical feedstock in the leather industry

#### Materials and methods

Humps Hachi fat was delivered from a medium local slaughterhouse. Chrome tanned leather of a thickness of 2- 4 mm was delivered from a medium tannery. Commercial sodium lauryl sulfate has been used as a wetting agent. Sodium metabisulfite  $Na_2S_2O_5$  has been used as sulfiting agent [8]. All chemicals used are fine grade and were purchased from international markets.

#### 2-1 Hump fat sulfitation

An Appropriate amount of camel hump fat has been heated in a stainless-steel autoclave, the temperature was set at 75 °C, the melted fat was treated with a saturated solution of sodium metabisulfite (1.5 mole / Kg, based on the weight of fat) dropwise under continuous stirring under current airflow. After two hours of stirring time, the mixture was cold to room temperature. The cold fatty matter was then washed and separated by salting out technics and neutralized to PH 6-7 using 20% aqueous sodium bicarbonate solution, the sulfited fat has been stored in sealed containers for further evaluation [8, 9]

#### 2-2 Evaluation of the sulfited fat

The progress in sulfition reaction and sulfited fat formation was investigated through measuring acid value, organically  $SO_3\%$ , and the decrease in iodine value [10] [11].

#### 2-3 Evaluation of the fatliquor emulsion stabilities

The fatliquor emulsion has been formulated by slowly adding 10 % sulfited fat followed by 1.5 % commercial sodium lauryl sulfate as a wetting agent (based on the weight of water) into hot water (60  $^{\circ}$  C) under contentious stirring for 30 minutes until homogenous mixture formation. The fatliquor emulsion stability has been measured against metallic ions [12] and pH variation [13], therefore the stability of the emulsion against the acidity of the medium indicates its good performance. Fatliquor emulsion (10%., sulfited fat in water) has been built as milky appearance emulsion. For testing the stability against acid; about two ml of formic acid HCOOH was added to 20 ml of the emulsion of the lubricant. For testing the stability against bases; 2g of NaHCO<sub>3</sub> was completely dissolved into 20 ml of the emulsion. After well shaking the emulsions, their aspects as homogenous, non-homogenous or oil separation have been detected over half-hour.

#### 2-4 Fatliquoring process

The chrome tanned bovine leather samples (wet blue) have been cut into small pieces of 5x5 cm2 surface area, the leather pieces were well soaked into freshwater for 60 minutes. The water has been tapped out and the leather pieces have been treated with sodium format solution and stirred for 15 minutes followed by treatment with sodium carbonate and stirred for further 15 minutes until gave greenish-blue color through the whole leather thickness with bromocresol green to adjust pH value to 5.5-6 [14, 15]. The mass of the samples has been verified and recorded. The neutralized leather charged into a wood container equipped with stirring rods and a heater. The leather was mixed with 500 % floating water and 10 % sulfited fat, based on the weight of fatliquored leather. The contents have been moved for 90 min (50 rpm stirring time) at 60 °C. After that, the liquoring liquid is tapped out and the fatliquored leather pieces have been droop up in open air until the whole drying [16].

#### 2-5 Evaluation of the fatliquored leather.

The quantity of oil added to fatliquored leather was evaluated via Soxhlet extraction of the introduced fat from the fatliquored using an organic solvent [15, 17]. The mechanical properties enhancement (elongation % at and break Tensile strength) have been evaluated. The morphology test of leather fibers has been studied by scanning electron microscope SEM, the leather samples were coated by gold ions so the images of the fibers before and after fatliquoring can be compared.

#### 3- Results and discussion

### 3-1Evaluation of the sulfited fat

The chemical properties of the treated hump fat have been illustrated in table 1, the degree of unsaturation that the fat possesses makes it respond to addition reactions, where the sulfite group can be introduced via addition reaction to act as hydrophilic heads, moreover, the significant saponification value of the fat confirms that it is a good oleochemical resource [18]. The remarkable decrease in the iodine value after the treatment give indication of the progress of the addition of sulfite ion and the successful fat sulfition, the high ratio of organically combined SO3 % confirm that the required amount of sulfite ion to formulate leather fatliquor  $\geq 5$  % has been recognized, and successful sulfition has been taken places [19].

#### 3-2 Evaluation of the emulsion stability

The liquoring process takes place up to 50 minutes and the emulsion has to be stable over this period of time. Breaking emulsion causes fat deposition on the surface leading to the formation of greasy leather. Moreover, the large oil droplets con not penetrate the surface causing failure fatliquoring. The fatliquoring bath may contain some metallic ions, the metallic ions react with hydrophilic heads forming insoluble salt resulting in emulsion separation [5] [20]. Therefore, the fatliquoring emulsion should possess significant stability against metallic ions to prevent breaking of the emulsion [1]. The data in table 2 shows that the fatliquor emulsion shows considered stability against different metallic ions incorporated in leather manufacture up to 2 hours' time period, which means the fatliquor doesn't suffer any breaking during fatliquoring process. The data in table 3 confirms that the prepared suflited fatliquor emulsion exhibits good stability against pH variation, the emulsion exhibits considerable emulsion stability up to 50 minutes without emulsion breaking or oil sepration. In general, the data revealed a good expectation of the highefficiency performance of the fatliquor emulsion.

Table 1: Chemical properties of sulfited hump fat

| Property                              | Un-sulfited | Sulfited |
|---------------------------------------|-------------|----------|
|                                       | fat         | fat      |
| Ash %                                 | 2.3         | 3.1      |
| Moisture%                             | 3.1         | 4.15     |
| Colour                                | white       | Pale     |
|                                       |             | yellow   |
| Iodine value mg I <sub>2</sub> /g oil | 62.74       | 18.00    |
| Saponification value mg               | 202.3       | 198      |
| KOH/ g oil                            |             |          |
| SO <sub>3</sub> %                     | -           | 5.19     |

Egypt. J. Chem. 65, No. SI:13 (2022)

Table 2: Stability of fatliquor emulsion against Metallic ions

| Metallic ion solution         | Stability        |  |
|-------------------------------|------------------|--|
| 5% basic chromium sulfat      | Stable up to     |  |
| (tanning liquor)              | 1.20 hours       |  |
| 5 % magnesium sulfate (hard   | Stable up to     |  |
| water)                        | 1.40 hours       |  |
| 5% sodium chloride +1.5       | Stable up to 2.1 |  |
| sulfuric acid (pickle liquor) | hours            |  |
|                               |                  |  |

Table 3: Stability of fatliquor emulsion against pH variation

| Time     | Aspects in  | Aspects in     |
|----------|-------------|----------------|
| (minute) | acid medium | basic medium   |
| 10       | stable      | stable         |
| 20       | stable      | stable         |
| 30       | stable      | stable         |
| 40       | stable      | stable         |
| 50       | partially   | partial        |
|          | decompose   | decompose      |
| 60       | oil         | oil separation |
|          | separation  |                |

#### **3-3 Fatliquored leather evaluation**

The ability of an emulsion to transfer fatty matter droplets into leather fiber represents a good parameter for the performance of the fatlliquor. Therefore, the mass added to the fibers promotes the sliding of fiber bundles and enhances the mechanical properties of the leather [18]. Figure 1 represents the relation between fatliquor concentration and the enhancement in the tensile strength and elongation at breaks %.





The data in the figure shows that there is a fatliquor proportional relation between the concentration and the enhancement into the tensile strength and elongation at breaks %. The gradual enhancement in tensile strength and elongation at breaks % with the increase of the fatliquor concentration confirm that the emulsion itself was able to add mass to the liquored leather, added mass increase as the fatliquor concentration increased confirm this. The relation between added fatty matter and emulsion of fat liquor concentration is illustrated in figure 2.



Fig.2: The relation between fatliquor concentration and fatty matter added to leather fiber.

The data in the figure shows the steady increase in the amount of fatty substance added to the liquored leather with the increase in the concentration of the emulsion, which confirms the data in figure 3 that the substance was added by the fatliquore emulsion, and the emulsion is able to transfer the fatty substance within the leather fibers. The morphology of the leather surface and leather fibers are shown in figures 5 (a & b).



Fig.3: Scanning electron microscope (SEM) of unfatliquored leather (a) SEM of fatliquored leather (b)

Comparing the two figures before and after the fatliquoring process, the significant improvement is evident, as it appears that the skin fibers were covered with a layer of fat, which indicates the success of the fatliquoring process and the fatliquor emulsion was able to add a fatty mass. Moreover, a remarkable enhancement in the visual appearance and softness of the fatliquored sample has been observed, confirming obtaining a good liquoring effect. Therefore, the prepared fatliquore exhibits the desired liquoring effect. The study succeeded in adding value to the camel hump fat by transferring it into a value-added product.

# CONCLUSION

An effective leather fatliquoring agent was formulated from hump camel fat via sulfition process,

the emulsion of sulfited hump fat shows great stability against different factors incorporated into the leather industry (metallic ions, and pH variation). The emulsion was able to add fatty matter into the tanned leather fiber, the fatliquor exhibits a high liquoring effect. The mechanical properties of the fatliquored leather samples are greatly enhanced, tensile strength and elongation at breaks are strongly enhanced, In addition to a noticeable improvement in softness and texture as well as the visual appearance. Value-added product (leather fatliquoring agent) has been formulated from camel hump.

#### Acknowledgment

This research was supported by the Deanship of Scientific Research, Imam Mohammad Ibn Saud Islamic University, Saudi Arabia, Grant No. (20-13-12-006). The authors gratefully acknowledge this support.

#### References

- Habib, M., Non-Chemically Modified Prefix Substance as A Fat Liquor for Leather Manufacture from Recovered Neatsfoot Oil. Egyptian Journal of Chemistry, 2017. 60(4): p. 667-674.
- Covington, A., Re: Tanning Chemistry: Science of Leather by Professor Tony Covington Reply. JOURNAL OF THE SOCIETY OF LEATHER TECHNOLOGISTS AND CHEMISTS, 2009. 93(6): p. 257-257.
- Saranya, R., et al., Synthesis of fat liquor through fish waste valorization, characterization and applications in tannery industry. Waste and Biomass Valorization, 2020. 11(12): p. 6637-6647.
- 4. Habib, М., **MODIFICATION** OF THE RECOVERED LOW-GRADE FAT TO FORMULATE **ECO-FRIENDLY** LUBRICANT GREASE. Latin American Applied Research-An international journal, 2018. 48(1): p. 69-74.
- Nyamunda, B., M. Moyo, and F. Chigondo, Synthesis of fatliquor from waste bovine fat for use in small scale leather industry. 2013.
- Mirgani, T., Fatty acid composition of hump triglycerides of the camel Camelus dromedarius. Comparative biochemistry and physiology. B, Comparative biochemistry, 1977. 58(2): p. 211-213.
- Sbihi, H.M., I.A. Nehdi, and S.I. Al-Resayes, Characterization of Hachi (Camelus dromedarius) fat extracted from the hump. Food chemistry, 2013. 139(1-4): p. 649-654.

- Haq, M.I.-U., et al., Synthesis, characterization and application of sulphited castor maleic adduct as an effective leather fatliquor. J Soc Leather Technol Chem, 2016. 100: p. 263-270.
- Habib, M. and A. Alshammari, Leather fatliquor from hide flestings. J. Soc. Leath Tech. Ch, 2014. 98(5): p. 199.
- 10. Mehlenbacher, V. and T. Hopper, American Oil Chemists' Society Official and Tentative Methods. The Analyst, 1958. **72**: p. 157.
- 11. Firestone, D., Official methods and recommended practices of the AOCS. 2009: AOCS.
- 12. Santos, L.M. and M. Gutterres, Reusing of a hide waste for leather fatliquoring. Journal of Cleaner Production, 2007. **15**(1): p. 12-16.
- Cuq, M., B. Benjelloun-Mlayah, and M. Delmas, Oil extracted from seal hides: Characterization and use as leather fat liquor. Journal of the American Oil Chemists' Society, 1998. 75(8): p. 1015-1019.
- 14. Nashy, E.S.H. and G.A. Abo-ELwafa, Highly stable nonionic fatliquors based on ethoxylated overused vegetable oils. Journal of the American

Oil Chemists' Society, 2011. **88**(10): p. 1611-1620.

- 15. Habib, M. and A. Alshammari, Recycling and utilization of waste deep frying oil in leather industry. 2017.
- 16. Kassahun, W., Preparation of leather fatliquor cum filler from fleshing waste for retanning process in leather manufacture. Addis Ababa University, 2014.
- Żarłok, J., et al., Research on application of flax and soya oil for leather fatliquoring. Journal of cleaner production, 2014. 65: p. 583-589.
- Ola, A., M. Habib, and N. El Sayad, Sulphitation of animal bone fat for use as a fatliquor. Journal of the Society of Leather Technologists and Chemists, 2014. 98(5): p. 205-210.
- Habib, M. and A. Alshammari, Leather fatliquor from hide flestings. Journal of the Society of Leather Technologists and Chemists, 2014. 98(5): p. 199-204.
- Kimbler, O.K., R. Reed, and I. Silberberg, Physical characteristics of natural films formed at crude oil-water interfaces. Society of Petroleum Engineers Journal, 1966. 6(02): p. 153-165.